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**Development and validation of DGT passive samplers for the quantification of Ir, Pd, Pt, Rh and Ru:
a challenging application in waters impacted by urban activities**

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Introduction

Platinum Group Elements (PGEs) comprise 6 elements: ruthenium, rhodium, palladium, osmium, iridium and platinum. These elements are among the least abundant in the terrestrial crust with concentrations ranging from 1 $\mu\text{g kg}^{-1}$ for Ir, Rh, Ru to 15 $\mu\text{g kg}^{-1}$ for Pd [1]. Thus, their natural concentrations in the environmental compartments are very low [2,3]. Moreover, these elements are characterized by low water solubility.

During the last decades, the use of PGEs (mainly rhodium, palladium and platinum) has increased significantly due to their utilization in automotive catalytic converters [3,4]. In the environment, enrichment of concentrations of PGEs has therefore been noticed due to the abrasion of these converters, releasing fine particles containing PGEs [5]. This phenomenon has been observed for all the compartments studied (*e.g.* snows, air, soils, sediments, etc...) [6-9]. Osmium has a different fate in the environment due to the formation of OsO_4 [10-12], a volatile specie. Other sources of pollution may exist especially for platinum [13,14], which is also used in medicine as cancerostatic drugs. The latter can indeed represent an important source of platinum in water, as these Pt-complexes (*e.g.* carboplatin, cisplatin and oxaliplatin) are more soluble than other species of platinum coming from catalytic converters mainly under oxide forms or metallic particles [13]. These three platinum-based drugs have been approved worldwide. Moreover, four other drugs are commercialized only in one country each: nedaplatin and miriplatin (both in Japan), lobaplatin (China) and heptaplatin (South Korea) [15,16].

In fresh and seawaters, the quantification of PGEs is really challenging because of their very low concentrations (generally below or close to the ng L^{-1}) and the bias introduced by possible analytical interferences. Many analytical techniques can be used for the determination of PGEs: Atomic Absorption Spectrometry, Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), X-Ray Fluorescence Spectroscopy, electrochemistry and Neutron Activation Analysis [17]. Among these techniques, electroanalytical techniques [18] and the various forms of ICP-MS (*e.g.* ICP-QMS, ICP-SF-MS, etc.) are the most commonly used in aquatic environments [19]. Both these techniques have limits of quantification below the ng L^{-1} but they are also sensitive to bias such as: (*i*) spectral interferences for ICP-MS (Table S1, see Appendix); and (*ii*) matrix effects for Adsorptive Cathodic Stripping Voltammetry induced by organic matter and specific electroactive species depending on the reagents and the electrodes used [20,21]. Thus, pretreatment steps are generally required to determine accurate concentrations.

For ICP-MS analyses, samples can be preconcentrated in laboratory using evaporation [22], solid phase extraction (SPE) [23], coprecipitation (*e.g.* with metalloid salts such as Te) coupled with isotopic dilution [24]. Less frequently liquid-liquid extraction or other techniques (*e.g.* electrochemical preconcentration, biosorption, etc.) may be used [24,25]. All these methods are time consuming, sometimes expensive, and can introduce contamination due to multiple steps procedure.

In situ techniques can also be used to preconcentrate species directly in sea or freshwater. It is the case of Diffusive Gradients in Thin films (DGTs) introduced by Davison and Zhang. This technique is now employed for a wide range of elements (*e.g.* nutrients, metals, organic compounds, etc.), matrices (*e.g.* soil, sediment, water) and applications (*e.g.* chemistry, ecotoxicology, biology) [26-29]. However, as PGEs are emerging contaminants, only one publication could be found in the literature about the use of such technique applied to these elements [30]. This paper is the second one on this issue with the additional consideration of iridium and ruthenium. These elements may be used as

cancerostatic drugs in the latter decades as clinical tests have already been performing with iridium or ruthenium-based drugs [31,32].

In this paper, two promising resins (a macroporous polystyrenic based chelating resin functionalized with thiouronium groups and an ammonium quaternary functionalized anion exchange resin) have been tested for the simultaneous detection of iridium, ruthenium, rhodium, palladium and platinum at ultra-trace levels using DGT sampling technique. Osmium was not considered in this study because of its particular fate in the environment. This element remains of interest for further development particularly due to its interesting isotopic signature. Performances of the resins have been tested through various parameters (*e.g.* adsorption rate, elution efficiency...). In addition, and for the first time, particular attention has been paid to the efficiency of the resins for the quantification of platinum-based cancerostatic drugs used worldwide (*i.e.* cisplatin, oxaliplatin, carboplatin). Finally, the first field application focused on wastewater treatment plants (WWTPs) effluents has been performed to validate the use of these DGTs devices in waters strongly impacted by urban activities.

2. Material and methods

2.1 Reagents

All solutions were prepared using ultrapure water (Milli-Q gradient, Millipore, $\rho = 18.2 \text{ M}\Omega \text{ cm}$). Mono-elemental standards used for the experiments focused on interferents were purchased either from SCP Science (Courtaboeuf, France) or from Courtage Analyses Services (Mont-Saint-Aignan, France). The stock PGEs multistandard solution used for calibration (Astasol, 100 mg L^{-1} in 20% HCl *v/v*) was obtained from SCP Science. The oxidation numbers of the PGEs in the stock solution are detailed in Table S2 (see Appendix).

Nitric acid (67-69%, optima and trace metal grade) was purchased from Fisher Scientific (Illkirch, France). Trace metal grade hydrochloric acid (35-38%), agarose low electroendosmosis for electrophoresis, NaCl (99%) and thiourea (>98%) were acquired from Merck (Darmstadt, Germany).

The resins tested were obtained from Strem Chemicals (Bischheim, France) for Deloxan® THP II Macroporous, Purolite® S-914 and S-920, from Magpie Polymers (Saint Pierre Les Nemours, France) for MPX-310 and MPX-317, from TrisKem International (Bruz, France) for Cl-resin, from Bio-Rad (Hercules, USA) for AG MP-1, from IBC Advanced Technologies (American Fork, USA) for Analig® PM-09, from Graver Technologies (Glasgow, USA) for Metsorb® and from Merck (Darmstadt, Germany) for Amberlite® CG-400, Dowex® 50WX8, 3-mercaptopropyl functionalised silica gel, Amberlite® XAD-4, Chelex® 100 and diethylenaminopropyl functionalised silica. Certified water SLRS-6 was purchased from the Canadian National Research Council (NRC-CNRC, Ottawa, Canada). All other chemicals used in this study were ACS reagent or analytical grade. Anticancer platinum-based drugs (solutions for infusion) which are cisplatin (1 mg mL⁻¹, excipients: water, NaOH, NaCl, HCl), carboplatin (10 mg mL⁻¹ in water) and oxaliplatin (5 mg mL⁻¹ in water) were produced by the company Accord Healthcare (Lille, France).

2.2 DGT preparation

2.2.1 Protocol of DGT preparation and treatment

The DGT pistons (DGT research Ltd.) have a diameter of 2.5 cm with a 2 cm diameter window allowing an exposed area of 3.14 cm². Both binding and diffusive gels were made using agarose at 2% w/w and 1.5% w/w respectively. Agarose gels were made by heating the solution until the complete dissolution of agarose. In order to obtain similar gel whatever the experiment, specific protocols have been set. Indeed, the pore size of agarose-based hydrogels is temperature dependent and the properties of the agarose gels can therefore change if constant conditions are not applied [33,34]. For the binding gel, immediately after casting the 2% w/w agarose solution mixed with the resin between two glass plates (e = 0.75 cm), the plates were left horizontally for 20 minutes at 60°C to ensure the decantation of the resin. The plates were then left horizontally at least 40 minutes at 4°C. For the diffusive gel, immediately after casting the 1.5% w/w agarose solution between two glass plates (e = 0.5 cm), the plates were left vertically at 4°C for at least 30 minutes.

After deployment of the DGT samplers (laboratory or field experiments), gel-resin disks were carefully recovered and introduced into 15 mL polypropylene tubes. PGEs were then eluted at 60°C for at least 48 h in a 1 mL mixture solution of 0.25 mol L⁻¹ thiourea / 0.25 mol L⁻¹ HCl or 0.5 mol L⁻¹ thiourea / 1 mol L⁻¹ HCl, respectively for AG MP-1 and S-920 resins. The choice of the elution solutions is explained section 3.1.2.

2.2.2 Preliminary studies and DGT laboratory experiments protocols

After determining the most suitable material for the vials (*i.e.* the least subject to PGE adsorption - see section 3.1.1), tests were performed in 25 mL high density polyethylene (HDPE) scintillation vials. Experiments (sections 3.1.2 - 3.1.3) were generally performed under stirring for 24 h with approximately 20 mg of resins (excepted for the selection of the resins where the protocol is detailed thereafter) in 20 mL of solution containing concentrations of PGEs of 50 or 100 ng L⁻¹. Experiments were first performed with resin as free powder then as powder incorporated in the agarose gel. Concentrations of PGEs remaining in solution were determined through two different protocols. In the case of free powder, solutions were filtered using acetate cellulose filters (0.45 µm) before acidification at 2% (v/v) with ultrapure HCl and thiourea (6.5-13 mmol L⁻¹). In the case of gel-resin disks, the disks were removed and the remaining solutions were stabilized by adding ultrapure HCl (up to 2% v/v) and thiourea (6.5-13 mmol L⁻¹). Note that the range of concentrations indicated for thiourea is due to its introduction as solid with the tip of a spatula. Blank samples were systematically performed to check concentrations of PGEs. pHs ranged from 6.0 to 8.6 according to the experiments. Experimental conditions are summarized in Table S3 (see Appendix).

For the determination of diffusion coefficients (section 3.2), experiments were performed at known temperatures in HDPE containers filled with 4 or 5 litres of solutions containing: (i) 10 mmol L⁻¹ NaNO₃ / 5 mmol L⁻¹ NaHCO₃; and (ii) 50 ng L⁻¹ of PGEs or 100 ng L⁻¹ of Pt in the case of Pt-based drugs. When other matrices have been used, the conditions are clearly specified. Generally, 15 DGT

samplers were introduced in the stirred solution. Aliquots of water were collected at each DGT retrieval with the aim to check and correct the concentrations of PGEs in the medium. These aliquots were stabilized with ultrapure HCl (up to 2% v/v) and thiourea (6.5-13 mmol L⁻¹).

2.2.3 Field study

Sampling sites were selected in order to ensure concentrations of Pt in the ng L⁻¹ range, compatible with a direct determination by ICP-MS. WWTPs of Marquette-lez-Lille (around 500,000 inhabitant equivalent; 50°40'41.4" N, 3°04'26.3" E) and Villeneuve-d'Ascq (around 100,000 inhabitant equivalent; 50°37'48.5" N, 3°11'01.8" E) were chosen to carry out the DGT samplers deployment. Both these WWTPs belong to Lille Metropolis (France) and are managed by Veolia. These two treatment plants discharge their effluents into the Marque River, already strongly impacted by urban pressures. The WWTP discharge at Villeneuve-d'Ascq can account for up to 36% of its flow as reported by Ivanovsky *et al.* [35]. By contrast, no data exists concerning the impact of the Marquette-lez-Lille WWTP on the Marque River. The field study was performed from 25 June to 9 July 2019. During this period, the DGT samplers were deployed for 14 days in the outflow effluents and five additional grab samplings were performed. DGTs samplers were washed regularly to limit biofouling.

The grab water samples were collected using 500 mL HDPE bottle previously acid-cleaned and rinsed with ultrapure water. Before each sampling, the bottle was rinsed 3 times with the WWTPs outflow effluents. The samples were filtered on site using an acetate cellulose membrane (0.45 µm of porosity) and were immediately stabilized with ultrapure HCl (up to 2% v/v) and thiourea (6.5-13 mmol L⁻¹) for analyses of PGEs, or acidified at 2% (v/v) using ultrapure HNO₃ for the quantification of interfering elements. The samples were stored at 4°C before analyses.

DGT samplers were deployed in triplicate for each resin on both sites. During deployment, water temperature was recorded every ten minutes using a submersible probe Aquatic 2 (Tinytag). Additional four DGT samplers for each resin were brought to the field, as blank samples, to discriminate accurately blank samples and experimental triplicate results due to DGT variability. After

retrieval, DGT samplers were thoroughly washed with ultrapure water. In the laboratory, DGT samplers were immediately disassembled, rinsed with ultrapure water and the resins were eluted.

2.2.4 Elemental analyses

Determination of Sr in WWTPs outflow effluents was performed using an inductively coupled plasma optical emission spectrometer (ICP-OES 5110 VDV, Agilent Technologies) calibrated using standard solutions. The concentration of the other interferents and the concentrations of PGEs were determined using an inductively coupled plasma quadrupole mass spectrometer (ICP-MS 7900, Agilent Technologies) equipped with a standard introduction system [borosilicate MicroMist concentric nebulizer (0.4 mL min^{-1}), quartz double pass spray chamber cooled at 2°C , quartz torch (2.5 mm ID) and nickel cones]. X-lenses were selected as ion optic configuration. High purity He ($> 99.999\%$) was used as collision gas in the octopole reaction system (ORS) to handle polyatomic interferences. Kinetic energy discrimination (KED) was also applied. Optimization in the laboratory was performed before analyses of PGEs and modes were settled to He flow at 4.5 mL min^{-1} and KED = 5 V for Rh, Pt and Ir, while for the other elements the mode used a He flow of 6 mL min^{-1} and KED = 5 V. Ion lens parameters were optimized daily. ^{74}Ge (for ^{63}Cu , ^{66}Zn , ^{85}Rb , ^{88}Sr , ^{89}Y), ^{115}In (for ^{101}Ru , ^{103}Rh , ^{105}Pd , ^{153}Eu , ^{157}Gd), ^{185}Re (for ^{178}Hf , ^{193}Ir , ^{195}Pt) and ^{205}Tl (^{208}Pb) were used as internal standards (ISTDs) from online addition of $50 \mu\text{g L}^{-1}$ stock solution in 2% (v/v) HNO_3 or HCl to correct potential matrix effects. Concentrations of ISTDs, after dilution in the samples, were around $3.4 \mu\text{g L}^{-1}$. Note that for the calibration curve of PGEs, dilution of the standard stock solution was performed in 2% HCl and 0.13 mmol L^{-1} of thiourea to increase the stability of PGEs [36]. This concentration was sufficient to prevent Pd from adsorbing on the walls of the 15 mL polypropylene tubes used for ICP-MS quantification. It allowed to pass QC tests. ISTDs corrected potential variations due to the higher amount of thiourea in the samples. Their recoveries were always included between 80% and 120%. SLRS-6 was used as material reference for performing quality control of the analysis when data were available. Limits of detection and quantification for PGEs are available in Table S4 (see Appendix).

3. Results and discussion

3.1 Preliminary tests

3.1.1 Adsorption tests onto materials

PGEs are known to adsorb easily on the walls of the containers and to be unstable even in HNO₃ acidified solutions [37,38]. Thus, preliminary stability experiments were performed over 1, 2 and 8 days in 6 different types of containers (*i.e.* glass, polypropylene, high density polyethylene, Pyrex[®] glass, quartz and polytetrafluoroethylene). Adsorption of PGEs was fast, within the first 24h and no significant differences could be observed between the different materials for Ru, Rh and Ir with recoveries ranging around 90 %. For platinum, the recoveries ranged from 65 to 75 % for all the materials tested. For palladium, polypropylene and glass exhibited the worst recoveries (around 10 % and 20 % respectively) while all the other materials allowed to obtain recovery close to 50 %.

HDPE vials were finally chosen for performing further experiments as these vials are easily disposable contrary to PTFE, quartz or borosilicate containers. This choice has been also made to avoid memory effects and constraining washing protocols. Note further that for the study of the resin properties, spiked samples without resins have always been prepared as control samples.

3.1.2 Characteristics of the resins

Selection of the resins and adsorption efficiency - Screening of resins for the accumulation of PGEs was performed without any modification of the commercial form (*i.e.* no drying step, no washing, no crushing). A wide variety of resins was tested: sulfur-based, nitrogen-based, phosphorus-based, and resin with no or unknown function as described in Table S5 (see Appendix). The experimental conditions are described in Table S3 (see Appendix). The adsorption efficiency was assessed by quantifying the concentration of PGEs remaining in solution by sampling 5 mL of solution after 24 hours. Samples were immediately acidified and stabilized with thiourea (6.5 – 13 mmol L⁻¹). The loss of Pd induced by the adsorption onto the walls was not corrected. Thus, the adsorption of Pd could

be overestimated in some cases. However, the adsorption of Pd was supposed to be similar for all resins and should not change the overall trend observed.

All the resins with less than 70% of adsorption for at least one element were discarded. In addition, resins with significant initial levels of contamination (after mineralization), not compatible with ultra-trace analysis (e.g. Deloxan® THP II), were also discarded. The results obtained have highlighted four resins that could be of interest for this study: S-920, S-914, AG MP-1 and CG-400. Even if MPX-317 revealed interesting adsorption properties, the adsorption was not good enough for platinum and palladium in the tested conditions (see Table 1) and therefore the resin was not further studied.

Before going further in the DGT development, a rapid elution test using HCl (1 mol L⁻¹) and thiourea (0 to 0.5 mol L⁻¹) was carried out with the aim to evaluate the elution capability of the resins. S-914 was also discarded as the elution was not much quantitative under these mild conditions compared to S-920. Abdulbur-Alfakhoury *et al.* [30] also showed that thiourea and HCl were not strong enough for recovering the PGEs from S-914. Besides, CG-400 and AG MP-1 showed very close adsorption and elution efficiencies due to their similar function. Thus, only one resin was selected for performing further tests. S-920 and AG MP-1 resins were finally selected as the most promising resins for the rest of the study.

Table 1: Adsorption of Ru, Rh, Pd, Ir and Pt onto several resins in Saint Amand® mineral water, at pH = 7.0 and spiked with 50 ng L⁻¹ of PGEs.

Resin	Adsorption Ru (%)	Adsorption Rh (%)	Adsorption Pd (%)	Adsorption Ir (%)	Adsorption Pt (%)
S-914	100 ± 1	94 ± 1	90 ± 2	98 ± 1	99 ± 1
S-920	99 ± 1	94 ± 1	88 ± 2	100 ± 1	99 ± 1
MPX-310	18 ± 11	64 ± 3	24 ± 9	97 ± 1	70 ± 2
MPX-317	85 ± 2	94 ± 1	40 ± 5	98 ± 1	45 ± 3
Dowex®	11 ± 14	0 ± 7	72 ± 4	0 ± 5	0 ± 5

50WX8					
Chelex® 100	30 ± 9	17 ± 11	76 ± 3	7 ± 12	9 ± 12
AG MP-1	86 ± 2	92 ± 1	76 ± 3	98 ± 1	90 ± 1
CG 400	96 ± 1	93 ± 1	83 ± 2	100 ± 1	95 ± 1
Mercapto-Si	22 ± 10	8 ± 12	91 ± 3	3 ± 12	83 ± 2
Deloxan® THP II	96 ± 1	89 ± 1	80 ± 4	66 ± 2	99 ± 2
Cl Triskem	7 ± 11	0 ± 23	87 ± 3	1 ± 17	64 ± 7
XAD-4	69 ± 5	15 ± 12	77 ± 3	8 ± 11	72 ± 4
DET Si	60 ± 6	74 ± 4	50 ± 7	96 ± 1	84 ± 2
PM09-Si	37 ± 9	61 ± 5	19 ± 12	90 ± 1	38 ± 8
Metsorb®	96 ± 1	61 ± 7	65 ± 5	1 ± 17	86 ± 2

Uncertainties represent the standard deviation of the measurements and replicates ($n = 3$).

Influence of pH and the concentrations of chloride ions on the adsorption efficiency - The effect of pH (and concentration of chloride ions simultaneously) on the complexing capacity of the two selected resins was investigated by changing the concentration of HCl in the solutions. In addition, fresh and 1-week aged solutions of PGEs were considered to determine if a potential change of speciation as a function of time could affect the adsorption efficiency of the resins [39]. The change of speciation was mainly expected to involve three types of reactions: *i*) aquation reactions consisting of the replacement of chloride ligands by water molecules, *ii*) hydrolysis allowing the formation of OH⁻ from H₂O ligand and *iii*) the possible replacement of chloride ligands by carbonate ligands. The aquation reactions undoubtedly take place even in the standard PGEs solution acidified at 3 mol L⁻¹ of HCl. Under these conditions, the main complexes for Pd, Pt and Ir are still the fully chlorinated complexes (respectively PdCl₄²⁻, PtCl₆²⁻ and IrCl₆²⁻) [40-42]. Concerning Ru and Rh, the dominant species are supposed to be Ru(Cl)₅(H₂O)²⁻ and Rh(Cl)₅(H₂O)²⁻ respectively considering Ru(III) and Rh(III) [43,44]. Aquation reactions occur faster for Ru(III) followed by Rh(III) and finally Ir(III) which is the least

impacted element [45]. Moreover, the less chloride ligands remaining, the slower the aquation is. The oxidation state of Ir can change in chloride media [46]. The reactions of PGEs (hydroxy)chlorocomplexes with carbonate ions are not well documented in literature. However, these reactions have been shown to occur with anticancer drugs and can also be expected with other complexes of PGEs [47-49]. The results for the adsorption over 24 hours are described in Figure 1.

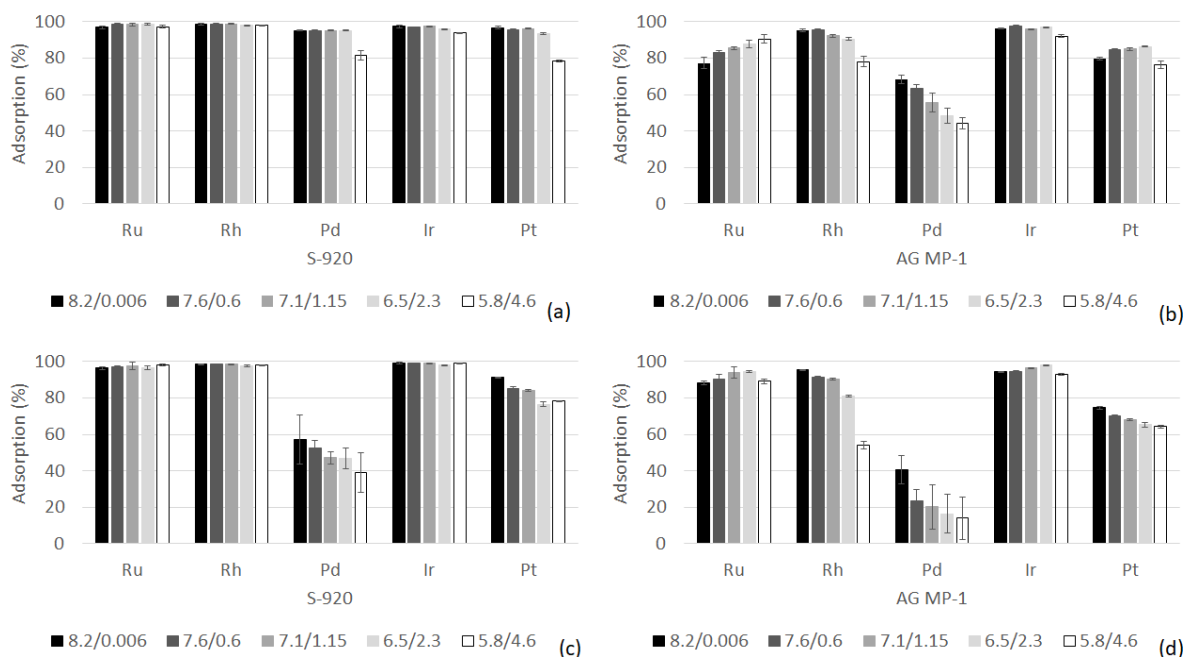


Figure 1: Adsorption of PGEs according to pH/[Cl⁻] (mmol L⁻¹) in the samples for: (a) S-920 in fresh solution; (b) AG MP-1 in fresh solution; (c) S-920 in aged solution; and (d) AG MP-1 in aged solution. Error bars represent the standard deviation of the measurements and replicates ($n = 3$).

Concerning S-920, Ir, Ru and Rh were impacted neither by the solution aging nor by the pH change. Indeed, more than 90% of these elements were adsorbed whatever the tested conditions. Concerning Pt and Pd, adsorption was found to decrease when the solution was aged one week before introducing the resins discs. Such decrease could be associated to an irreversible adsorption onto the wall of the vials as shown in section 3.1.1. In fresh solution, pH and/or the concentrations of chloride ions did not have a significant influence except at pH = 5.8 for which a 15 to 20% decrease of adsorption was observed. The mechanism of complexation by S-920 should mainly involve chelation

processes through the thiuronium functional group that contains both nitrogen and sulphur atoms but was not studied in depth here. In the literature, this mechanism of complexation is not precisely described either. It is also possible that ionic interactions or hydrogen bonding may play a role in the process of complexation depending on the exposure conditions [50,51]. The decrease in adsorption observed for Pd and Pt can be related to a change in the surface charge of the resin since the zero charge point and the isoelectric point were determined at pH 6.5 and 5.9 respectively [50].

For AG MP-1, the recoveries were less promising for all the PGEs. Adsorption obtained for Ru, Rh and Ir were generally higher than 80% whatever the aging time, except for Rh at pH = 5.8 for which the percentages of adsorption were lower (around 75% and 55% respectively for non-aged and aged solution). As for S-920, Pd and Pt adsorption in the aged solutions were lower than in the fresh solutions. Pd seemed also impacted by the diminution of the pH or/and the increase of the concentration of chloride ions. Finally, AG MP-1 resin appears to be more sensitive than S-920 resin to pH and the concentration of chloride ions. The mechanism of binding for AG MP-1 was not investigated in this study but is likely to be based on ion exchange [52,53]. The resin was used already under its chloride form so the differences observed were not expected to come from anion exchange with chloride. The difference of adsorption should mainly be due to the above-mentioned changes of speciation. Indeed, for Ir no difference was observed between fresh and aged solution probably due to the low kinetics of the aquation reactions with this element. By contrast, differences were observed for Ru and Rh with different trends. On the one hand, higher concentration of chloride ions could slow down the aquation reactions, on the other hand higher concentration of chloride ions was coupled with lower pHs that potentially slowed down hydrolysis.

Adsorption isotherms - Adsorption kinetics of PGEs onto the resins must be studied for DGT development. The experiments lasted 24 hours and the results are displayed in Figure 2.

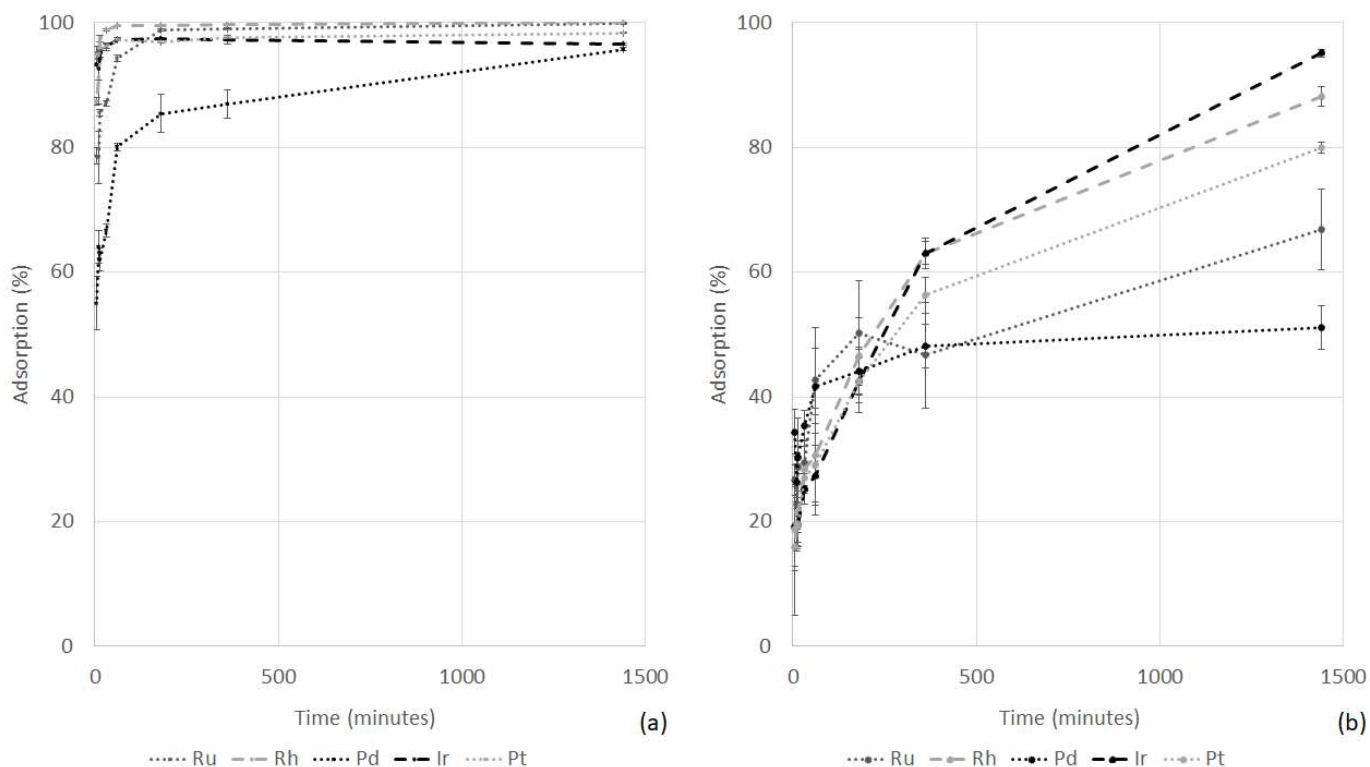


Figure 2: Adsorption isotherms for PGEs onto S-920 and AG MP-1 resins at 25°C. Error bars represent the standard deviation of the measurements and replicates ($n = 3$).

As observed by Abdulbur-Alfakhoury *et al.* [30], the adsorption kinetics of the S-920 resin were really fast within one hour for all the elements except for Pd where 20% still remained in solution. Note that the matrices and the concentrations tested in the present study are different than those used by Abdulbur-Alfakhoury *et al.* [30] (*i.e.* simple matrix - $\text{NaNO}_3 / \text{NaHCO}_3$ solution described in Table S3 (see Appendix) - spiked at 50 ng L^{-1} of PGEs in this study *versus* artificial seawater spiked at 1 mg L^{-1} of PGEs for the previous study). Conversely, AG MP-1 was found to accumulate PGEs slower than S-920. After 24 hours of contact, the adsorption rate was still acceptable (above 80%). Finally, even if adsorption kinetics for AG MP-1 were not as fast as expected, this resin still remained interesting for the preparation of DGT because in natural waters, with concentrations of PGEs at least 10 times lower, other kinetics in DGT samplers may be more limiting (*e.g.*, decomplexation reactions) and the competition with other interfering species has not yet been studied (see section 3.3 for the results).

Optimization of the elution conditions and determination of the elution factors - Elution of the resin is an important step for the development of DGT. This elution should be comprised between 75 and 100% [27]. Contrary to Abdulbur-Alfakhoury *et al.* [30] who used aqua regia, it was decided to use milder elution conditions. Thiourea/HCl mixtures are well known for the elution of PGEs and have been considered as the most promising ones in our case [54-46]. Additional tests using EDTA and potassium thiocyanate (KSCN) were also performed, but in both cases, the recoveries were lower than those obtained using mixtures of thiourea and HCl (data not shown). The optimization was conducted by screening several concentrations of HCl (from 0.25 to 3 mol L⁻¹), thiourea (from 0.25 to 0.75 mol L⁻¹) and several temperatures (from 20 to 80°C). For AG MP-1, few differences were observed on the elution efficiency except at 80°C, temperature for which Pd and Pt were less desorbed with a loss of more than 80% and 30% respectively, compared to the same elution solution with the temperature set at 60°C. Elution factors were determined by letting resin gel adsorbing PGEs during 24 hours in a solution described in Table S3 (see Appendix). Amounts of PGEs adsorbed were determined by comparing spiked samples with and without resins after 24 hours. Solutions were acidified and stabilized with thiourea (6.5 – 13 mmol L⁻¹) after the withdrawal of resin gels. Resin gels were withdrawn, rinsed with ultrapure water and eluted with 1 mL of solution.

Conversely, the desorption process for S-920 resin was found to be more affected by the elution conditions (Figure S1, see Appendix). Indeed, the elution efficiency was highly temperature-dependent with optimal performance found at around 60°C. As for the AG MP-1 resin, the percentage of recovery decreased at 80°C, especially for Pd, and to a lesser extent for Pt. Increasing the concentration of HCl from 0.25 to 1 mol L⁻¹ provided a slightly better elution efficiency for all the elements. The benefits were however not significant when the concentration was increased from 1 to 3 mol L⁻¹. Concerning thiourea, the increase of concentration from 0.25 to 0.5 mol L⁻¹ resulted in significant improvement of the desorption for Ru and Pd. However, the increase of the concentration of thiourea up to 0.75 mol L⁻¹ did not improve significantly the elution.

Based on these results, it was decided to perform the elution of PGEs using a 0.25 mol L⁻¹ thiourea/0.25 mol L⁻¹ HCl solution for AG MP-1, and a 0.5 mol L⁻¹ thiourea/1 mol L⁻¹ of HCl solution for S-920. Both elutions were performed at 60°C for at least 48h. The elution factors (f_e) found are compiled in Table 2. Note that f_e for Ir is quite low using S-920 and for this element, the AG-MP1 resin is more adapted.

Table 2: Average elution factors (f_e) obtained for PGEs ($n = 20$). As Pd was hardly adsorbed by AG MP-1 elution factor was not calculated for this resin (N.D.: not determined due to low adsorption).

	Ru	Rh	Pd	Ir	Pt
f_e S-920	0.90 ± 0.04	1.00 ± 0.06	1.01 ± 0.08	0.54 ± 0.05	1.06 ± 0.05
f_e AG MP-1	0.94 ± 0.08	1.10 ± 0.06	N.D.	1.05 ± 0.03	0.98 ± 0.04

Uncertainties represent the standard deviation of the replicates.

3.1.3 Choice of the diffusive gel and filter for the DGT samplers

As shown in section 3.1.1, PGEs, and particularly Pd, can be easily adsorbed onto different surfaces. Thus, it is likely that palladium may also be trapped in the diffusive gel. Generally, DGT devices can be settled with 3 types of gel: (i) polyacrylamide made with a patented agarose-based cross-linker furnished by DGT® Research (Lancaster, United Kingdom) (APA); (ii) polyacrylamide with *N, N'*-methylenebis(acrylamide) as cross-linker also called restrictive gel (RG) and (iii) pure agarose gel (AGE). Adsorption of PGEs into these gels was studied by using spiked solutions with 50 or 500 ng L⁻¹ of PGEs and by calculating the recoveries of PGEs for each type of gel. Palladium was the most impacted element, whatever the gel tested, in the following order RG > APA > AGE. This observation, in adequacy with those reported before [30], could be partly explained by the Pearson's Hard and Soft Acids and Bases (HSAB) theory. As a soft acid, palladium should easily interact with the NH₂ (hard base) and C=O (soft base) functions of polyacrylamide. To a lesser extent, rhodium was also impacted by the type of gel with the same order than that observed for Pd. According to Horsfall and Spiff [57], Pt is supposed to be a softer acid compared to Pd and Rh. As a consequence, Pt should be only involved in soft-soft interactions with the RNH₂ functions while Pd and Rh could also be retained

by C=O functions explaining their similar behavior. However, this explanation is only given as hypothesis because the oxidation states of the elements in this study [Pd(II), Pt(IV), Rh(III) (Table S2, see Appendix) are not the same as those studied by Horsfall and Spiff [Pd (II), Pt (II), Rh(II)] [57]. According to the same authors, ionic radii could also be parameter to be considered to explain the adsorption properties of these elements.

Several filter materials were also tested for the preparation of the DGT samplers [*i.e.* mixed cellulose ester, cellulose acetate, polycarbonate, nitrocellulose, polyvinylidene fluoride (PVDF) and polyethersulfone (PES)]. The filters were left 24h in solution containing 50 ng L⁻¹ of PGEs at room temperature and the concentration of PGEs remaining in solution was determined by ICP-MS. PVDF showed the worst results with only 57% and 35% of remaining Pd and Pt respectively. To a lesser extent, polycarbonate and nitrocellulose filters showed affinity for PGEs (respectively 70% and 80% for the recovery of Pd vs 85-95% for the other filter types). Based on these observations, agarose diffusive gel and cellulose acetate filters were finally selected for the assembly of DGT dedicated to PGEs.

3.2 Determination of the diffusion coefficients.

Diffusive gradients in thin films technique was introduced by Zhang and Davison in 1994 to allow the assessment of trace metal speciation in environment [26]. Based on Fick's laws, the diffusion coefficient of a specie can be determined using the following equation (Eqn 1):

$$D = \frac{M \cdot \Delta g}{C_{batch} \cdot t \cdot A} \quad (\text{Eqn 1})$$

With D: the diffusion coefficient (cm² s⁻¹); M: the mass accumulated (g); Δg: the thickness of the diffusive layer (filter + diffusive gel = 0.062 cm in this study); A: the exposed area (3.14 cm²) and C_{batch} the concentration of PGEs in the batch (g cm⁻³).

Diffusion coefficients are also dependent on the temperature. Generally, the values are given at a temperature of 20°C or 25°C [58]. For correcting diffusion coefficients during this study, the Stokes-

Einstein law (Eqn. 2) was used in combination with the evolution of the viscosity as a function of temperature (Eq. 3).

$$\frac{D_{298K} * \eta_{298K}}{298} = \frac{D_T * \eta_T}{T} \quad (\text{Eqn. 2})$$

With T: the temperature of the experiment (K); D_{298K} and D_T : the diffusion coefficients at 298K and T, respectively ($\text{cm}^2 \text{s}^{-1}$); η_{298K} and η_T : the water viscosity at 298 K and T, respectively (Pa s).

$$\log\left(\frac{\eta_{298}}{\eta_T}\right) = \frac{1.37023(T-298)+0.000836(T-298)^2}{T-164} \quad (\text{Eqn 3})$$

3.2.1 Diffusion coefficients in simple matrices solutions

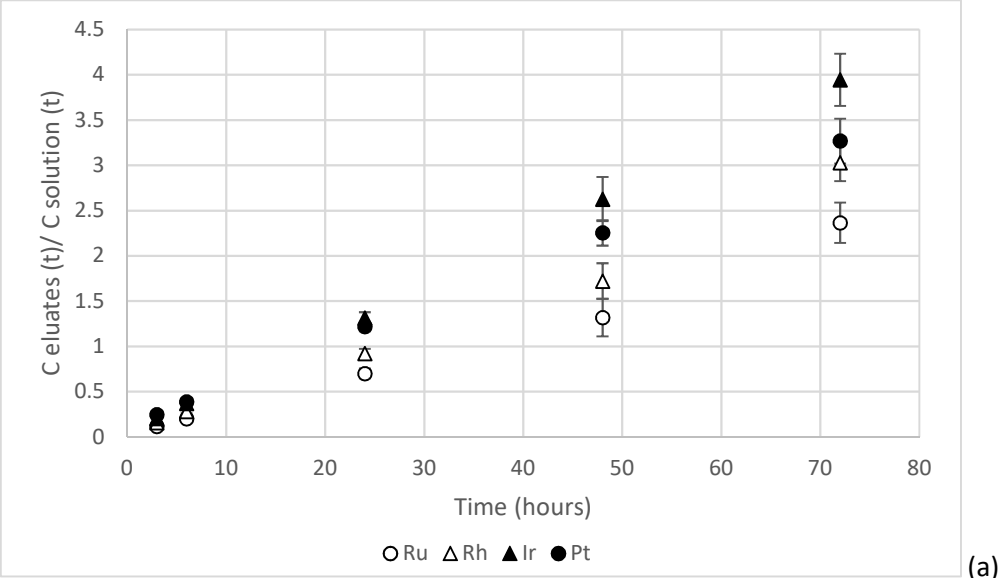
Using a simple matrix composed of 10 mmol L⁻¹ NaNO₃ / 5 mmol L⁻¹ NaHCO₃, the diffusion coefficients of PGEs were determined. Exposition times varied from 24 to 72 hours. Experiments were performed three times for AG MP-1 and S-920. The mean values of diffusion coefficients are displayed in Table 3. Values obtained by Abdulbur-Alfakhoury *et al.* [30] for the S-920 resin are indicated for comparison.

Table 3: Diffusion coefficient determined at 25°C ($10^{-6} \text{cm}^2 \text{s}^{-1}$).

	Ir	Pd	Pt	Rh	Ru
AG MP-1 NaNO₃ matrix (3.2.1)	6.0 ± 0.4	N.D.	4.8 ± 0.3	5.4 ± 0.1	4.3 ± 0.8
S-920 NaNO₃ matrix (3.2.1)	N.D.	5.4 ± 2.0	5.9 ± 0.6	3.7 ± 0.4	3.4 ± 0.3
AG MP-1 Saint Amand (3.2.2)	5.0 ± 0.1	N.D.	4.3 ± 0.2	3.9 ± 0.3	3.4 ± 0.5
S-920 Saint-Amand (3.2.2)	N.D.	4.3 ± 1.6	5.8 ± 0.2	3.7 ± 0.3	2.6 ± 0.2
S-920 seawater ^[30]	N.A.	4.87 ± 0.83	5.56 ± 0.55	2.29 ± 0.55	N.A.
S-920 river water ^[30]	N.A.	4.20 ± 0.32	4.99 ± 0.43	3.30 ± 0.24	N.A.

N.A stands for Not Available. N.D. stands for Not Determined. Uncertainties for the diffusion coefficients come from the uncertainty of the slopes for the accumulation of PGEs along time.

The results obtained for S-920 resin in simple matrices were closed to those obtained by Abdulbur-Alfakhoury *et al.* [30] in freshwater and seawater. Strong uncertainties can be noticed for the diffusion coefficients of Pd using S-920. The diffusion seemed to increase as a function of the time leading to a not fully linear relationship with R^2 from 0.95 to 0.99 according to the experiments (Figure 3). This observation, not previously reported in the literature, may be linked to the adsorption process of Pd on the walls (even if corrected) and/or the evolution of Pd reactivity with time. It is also possible that Pd can be slowed down by the filter and the agarose gel through a slight adsorption process before reaching a steady state. Overall, even if the AG MP-1 resin showed a slow adsorption kinetic, that did not seem to affect the whole accumulation process in the passive sampler.



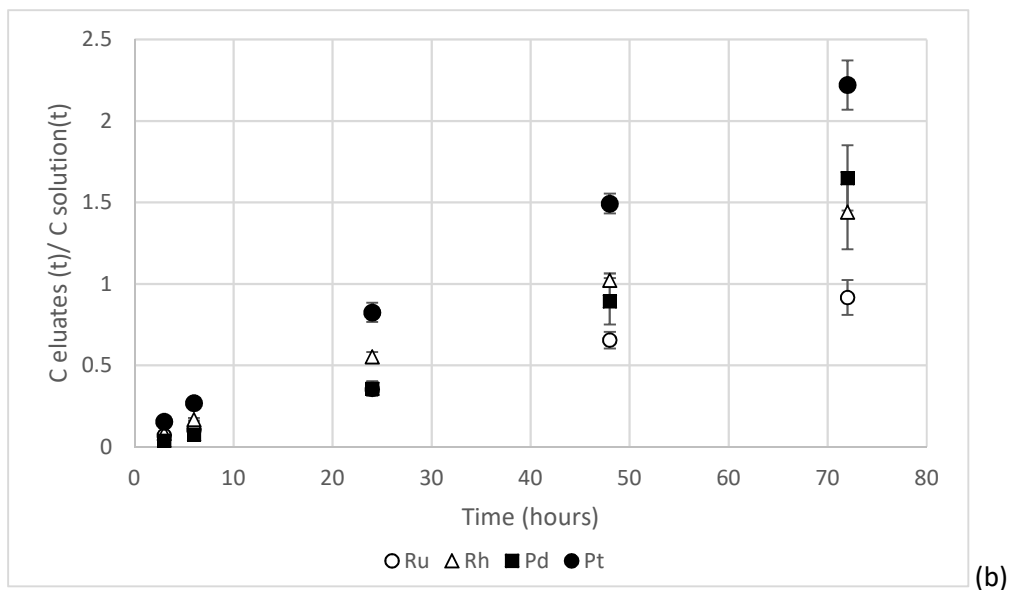


Figure 3: Accumulation of PGEs as a function of time in Saint Amand®: (a) with AG MP-1; (b) with S-920. Error bars represent the standard deviation of the replicates ($n = 3$).

3.2.2 Diffusion coefficients with Saint Amand® mineral water

An additional experiment was carried out using Saint Amand® mineral water, which composition is close to that of freshwaters from Northern France. The diffusion coefficients are indicated in Table 3. The experiment was performed once for both resins over 72 hours. Except for Pt and Rh with the S-920 resin, diffusion coefficients decreased significantly (Ir and Rh for AG MP-1 and of Ru for S-920). Letting aging the solution of PGEs during 48h instead of 12h period before introduction of the DGT samplers, also conducted to a decrease of the diffusion coefficients (Table S6, see Appendix). These results demonstrate that even in mineral water matrices, with low salinity and low organic matter content, a change of speciation can occur leading to a decrease of their accumulation in DGT samplers, through kinetic and/or thermodynamic considerations. Indeed, PGEs are introduced as (hydroxy)chlorocomplexes, which could be predominant at acidic pH according to Colombo *et al.* [59]. The aquation/hydrolysis of these (hydroxy)chlorocomplexes can occur at neutral or near neutral pH [37].

Three natural filtrated waters, sampled in lakes or river from Northern France, have also been tested. Logically, the diffusion coefficients decreased compared to simple matrices, indicating that dissolved

organic matter and/or colloids (dissolved organic carbon values ranging from 3.7 to 6.9 mgC L⁻¹) modify the speciation and therefore the diffusion and adsorption of PGEs in the passive sampler (Table S6, see Appendix).

These preliminary results confirm the interest of using DGT passive sampling as indicator of the bioavailable fraction of PGEs in the aquatic ecosystems when comparison with total concentrations is possible. The use of two resins like AG MP-1 or S-920 may also be a way to evaluate the possible species of PGEs present in the environment as the resins appear to exhibit different behavior of adsorption. This determination method is already employed for other elements like As [60,61] or Hg [62,63]. However, this strategy would imply to know exactly the species adsorbed by the resin which is not the case here. Moreover, DGT sampling can also take into account PGEs as nanoparticle species [64] as such particles are expected to pass through the diffusive gel. This further complicates the determination of the speciation of PGEs due to the possible presence of PGEs nanoparticles originating from catalytic converters abrasion [65,66]. Finally, Pt-based drugs further complicate the speciation of Pt by introducing other metabolites and complexes in the environment. The diffusion coefficients of these species have been investigated in the following section.

3.2.3 Diffusion coefficients of platinum-based drugs in simple matrices

The aim of this section is to determine in what extent platinum-based drugs (carboplatin, cisplatin, oxaliplatin) can be adsorbed onto the selected resins and if differences exist between the resins. Each drug was studied separately. The batches were left aging 24 hours with platinum-based drugs (100 ng L⁻¹ Pt equivalent) to match, as closely as possible, realistic conditions. Indeed, the drugs are not discharged directly into the aquatic systems due to their retention time in human bodies and in wastewater treatment processes. Simultaneously, batches of 20 mL with only the resin gel were prepared to estimate the percentage of adsorption of the drugs in the same matrix than those used for the 4 liters batches. Elution factors were determined for the three anticancer drugs studied. For both resins (2 replicates for each drug) elution factors were found between 0.9 – 1.1 as for Pt (IV).

From the results summarized in Table 4, it can be observed that the AG MP-1 resin was far less efficient for the adsorption of platinum-based drugs than the S-920 resin. Diffusion coefficients ranged from 0.25 to 0.4 $\cdot 10^{-6}$ $\text{cm}^2 \text{s}^{-1}$ for AG MP-1 compared to 1 to 4.1 $\cdot 10^{-6}$ $\text{cm}^2 \text{s}^{-1}$ for S-920. For both resins, the values were lower than those of (hydroxy)chlorocomplexes species. That point raises the question of the choice of the diffusion coefficients to be used for environmental monitoring because, in the rivers strongly impacted by urban pressures, most of dissolved Pt come from these drugs. Indeed, the concentrations would be highly underestimated if the diffusion coefficients related to (hydroxy)chlorocomplexes are chosen. However, it implies to know which drugs (their percentage and their metabolites) are used by surrounding hospitals. The selectivity of different resins for the determination of Pt fluxes in rivers could probably make possible to determine the origin of Pt. It might also be interesting to screen other promising resins for Pt determination to see if better adsorption could be found for Pt-based drugs.

Table 4: Percentage of adsorption of the Pt-based anticancer drugs onto the S-920 and AG MP-1 resins over 24 hours and their diffusion coefficients at 25°C ($\cdot 10^{-6}$ $\text{cm}^2 \text{s}^{-1}$).

	Carboplatin		Cisplatin		Oxaliplatin	
	AG MP-1	S-920	AG MP-1	S-920	AG MP-1	S-920
Indicative adsorption	12	29	26	48	8	82
Diffusion coefficient	0.25±0.1	1.0±0.3	0.39± 0.07	1.9±0.6	0.28±0.06	4.1±0.6

Uncertainties for the diffusion coefficients come from the uncertainty of the slopes for the accumulation of PGEs along time.

Moreover, this study gives information on the behavior of Pt drugs in the environment. Generally, carboplatin is considered as the most stable substance, followed by cisplatin and oxaliplatin; which can easily form a large number of molecules mainly due to their biodegradation [67]. Turner and Mascorda have shown that in riverine water, cisplatin is the most reactive compound with particulate matter followed by carboplatin while oxaliplatin is almost unreactive [68]. For both resins cisplatin was more adsorbed by the resin than carboplatin. Meanwhile, oxaliplatin was well adsorbed by S-920 resin but not by AG MP-1 during the DGT experiments. Then, it should be interesting to

understand in which forms the drugs are adsorbed onto the resins by a speciation approach such as HPLC-ICP-MS [69,70]. Finally, it may be surprising to observe adsorption on the AG MP-1 resin as platinum-based drugs are expected to be neutral species or to have a positive charge if only aquation or hydrolysis reactions occur. Some studies in the literature [47,48] have also shown that a replacement of the chloride or hydroxide ligand by carbonates is possible in the human body. Since the pHs and the concentration of (hydrogeno)carbonate ions in the batches were close to those observed in the human body, negatively charged complexes could be formed. S-920 was expected to react in the same way than Pt-based drugs on DNA adducts even if a study as shown that when carbonates were present, all the Pt was not reactive [47].

3.3 Selectivity of the resins

In order to study the adsorption of the potential spectral interferences (towards ICP-MS analyses) onto the resins, simple matrix solutions were spiked at $1 \mu\text{g L}^{-1}$ of Eu, Gd, Hf, Rb and Y; $10 \mu\text{g L}^{-1}$ of Cu, Pb, Zn and 1mg L^{-1} of Sr. Accumulation of the interferences in the DGT samplers was monitored for 3 days with a mean temperature of approximately 18°C . Accumulation of the interferences for each resin is displayed in Figure S2 and S3 (see Appendix). For the AG MP-1 resin, the selectivity of the resin with respect to the anions present in solution was not studied. However, the provider gives the affinity of the resin for several anions [52]. Comparing the results from section 3.2.2 and Table S6 (see Appendix) it seemed that carbonate and sulphate ions present in Saint Amand® water did not modify the diffusion coefficients. The impact of nitrate ions should however be investigated in further studies.

For the two resins, Cu was the most accumulated interfering element. 98% and 38% of Cu present initially in solution were adsorbed on S-920 and AG MP-1 respectively after 24 hours of contact. By contrast, some interferences such as Rb and Sr did not accumulate significantly (less than 10% for both resins). Concerning S-920, almost all the elements were adsorbed over 85% with the exception of Hf (54%), Sr (5%) and Rb (10%). In the same time, elution factors were determined, resulting in

recoveries of all elements with values greater than 90%. For AG MP-1, a reverse trend was observed for the adsorption: interferents were hardly adsorbed (below 15%) with the exception of Hf (56%) and Cu (38%). Elution factors also shown that the elements were quantitatively desorbed. Based on these results and to simplify calculations for the diffusion coefficients, the elution factors were set to 1 for the elements displayed Table 5. This table summarizes the diffusion coefficients of the main interferents accumulated in the two resins.

For both resins, even if the concentration of Sr did not increase in the gels during the experiment, its concentration, in the eluates, was not negligible with values around $20 \mu\text{g L}^{-1}$. High concentrations of Sr have also been reported by Abdulbur-Alfakhoury *et al.* [30] who proposed a rinsing step of the gel using ultrapure water before performing elution. In our case, such a concentration was not problematic for the analysis of PGEs thanks to the collision/reaction cell (He mode) by contrast with Abdulbur-Alfakhoury *et al.* [30] who used HR-ICP-MS subjected to Sr interferences (*i.e.* $^{87}\text{Sr}^{16}\text{O}^+$ not resolved onto ^{103}Rh).

Generally, in comparison with Chelex[®] 100 [58], used for the adsorption of metals and rare earths, the diffusion coefficients of interfering elements using S-920 and AG MP-1 resins are lower. These results confirm that our selected resins are more efficient than Chelex[®] for not adsorbing the interferents of PGEs. Using S-920, only Cu and in a lesser extent Zn, have similar diffusion coefficients than those observed with DGT made with Chelex[®] 100 or diffusion cell experiments. The other coefficients are at least twice lower. For instance, adsorption of Pb on AG MP-1 is approximately 100-fold lower than the adsorption with Chelex[®] confirming the absence of affinity of AG MP-1 for Pb. When comparing our values with those of the literature (Table 5), one bias could be linked to the nature of the gel. However, as suggested by several authors, this bias is not really relevant for the metals considered here [27,71,72].

Table 5: Indicative diffusion coefficients in simple matrices of the interferent at 25 °C ($*10^{-6}\text{cm}^2\text{s}^{-1}$).

	Cu	Eu	Pb	Zn

S-920 (AGE)	6.3 ± 0.5	0.7 ± 0.4	2.7 ± 0.7	2.8 ± 0.4
AG MP-1 (AGE)	3.1 ± 0.4	0.8 ± 0.3	0.10 ± 0.03	N.D.
Chelex (APA)	6.3	5.4	9.9	4.4
Diffusion cell (APA)	6.2	N.A.	8.03	6.08

N.D. stands for not determined due to low adsorption. N.A. stands for not available. The type of the diffusive gel is indicated in brackets. Uncertainties for the diffusion coefficients come from the uncertainty of the slopes for the accumulation of PGEs along time.

To conclude, the S-920 resin is more sensitive to the presence of interferents than AG MP-1 for PGEs quantification by ICP-MS. Indeed, the diffusion coefficients of interferents onto the S-920 resin are sometimes higher (Cu) or similar (Zn, Pb) than those obtained for PGEs. For AG MP-1, only Cu shows a diffusion coefficient in the same order than the diffusion coefficients of PGEs. For Sr, even if AG MP-1 eluates present concentrations twice higher than in S-920 eluates, due to dilution. However, the reduction of its concentration by a factor 50 thanks to DGT samplers allowed to obtain negligible interference equivalent concentrations (IECs) induced by Sr. As collision/reaction cell could not totally overcome interferences, especially those induced by doubly charged ($^{206}\text{Pb}^{2+}$ on $^{103}\text{Rh}^+$), the AG MP-1 resin seems better suited for quantifying accurately PGEs in presence of high amounts of Pb and Zn. Tests assessing the impacts of major anions [nitrate, sulphate and (hydrogeno)carbonate ions] on the efficiency of AG MP-1 resin should however be investigated to validate this assessment.

3.4 Field study

3.4.1 Discrete sampling: concentrations of PGEs and interferents

During the two weeks of DGT deployment in the WWTPs outflows, 5 discrete samplings were performed. Regarding the concentrations of PGEs (Table 6), Ru concentrations were too low to be precisely quantified (*i.e.* high standard deviations). Ir could not be quantified directly (<LD) and Pt was present in relatively high concentrations probably due to the presence of platinum drugs. Finally, concerning Rh and Pd, the obtained concentrations should be taken carefully. Indeed, in a previous

field study, a good correlation between Rh and Sr (up to 95%) was observed. Sr is present in high quantity (around 1 mg L⁻¹) in this watershed and such concentration may lead to residual spectral interferences that cannot be completely solved by ICP-QMS. Thus, even if Rh and Pd can be present in WWTPs, discrete sampling does not allow to determine accurately their concentrations. The use of DGT probes is going to overcome this difficulty.

Table 6: Mean ($n = 5$) dissolved concentrations of interfering elements and PGEs (non-corrected) obtained during discrete samplings (ng L⁻¹). For concentrations of Rh and Pd under brackets are those calculated based on IECs.

	Villeneuve-d'Ascq (VA)	Marquette-lez-Lille (MLL)
Cu	223 ± 29	423 ± 106
Zn	45,600 ± 4,700	12,200 ± 4,100
Rb	21,600 ± 1,800	19,000 ± 400
Sr	1,144, 000 ± 37,000	777,000 ± 11,000
Hf	<4	<4
Pb	83.3 ± 1.9	434 ± 61
Ru	0.14 ± 0.05	0.07 ± 0.04
Rh	1.04 ± 0.10 (0.21 ± 0.10)	0.73 ± 0.10 (0.14 ± 0.14)
Pd	2.25 ± 0.44 (1.30 ± 0.44)	1.65 ± 0.32 (0.96 ± 0.32)
Ir	<0.036	<0.036
Pt	2.90 ± 0.20	11.4 ± 2.6

Uncertainties correspond to the standard deviation of the replicates.

Concerning interfering elements (Table 6), it was interesting to notice that their concentrations could be very different according to the WWTPs. Concentrations of Zn were quite high particularly in Villeneuve-d'Ascq (VA) WWTP. These results also showed that VA WWTP had less variable

concentrations of interfering elements than those quantified at Marquette-lez-Lille (MLL). As explained above, the main bias of concentrations of PGEs in this study was induced by Sr. However, it was necessary to check the concentrations of all the interferents to determine if they might perturbate the quantification of PGEs. IECs were determined by introducing a known volume of interferent and by checking the value obtained by ICP-MS for the target PGE species. These values are given in Table S7 (see Appendix).

Based on the results in Table S7 (see Appendix), it can be assumed that total concentrations of Rh did not exceed on average 0.21 ng L^{-1} and 0.14 ng L^{-1} respectively for VA WWTP and MLL WWTP. With the same deduction, total concentrations of Pd reached the maximum of 1.3 ng L^{-1} for VA WWTP and 0.96 ng L^{-1} for MLL WWTP. For the other PGEs, no IECs have been detected. These results confirm clearly that in our study case only Sr prevents an accurate quantification of Pd and Rh

3.4.2 Passive sampling with DGT probes: concentrations of PGEs and interferents

Concentrations of interfering elements (*i.e.* Ni, Cu, Zn, Rb, Sr, Y, Eu, Gd, Hf, Pb) were determined in the eluates of the DGTs probes. After the quantification of the interferents, their impacts on concentrations of PGEs were determined by adding a known concentration of interferent, corresponding to the concentrations found in our eluates, in a matrix HCl 2% v/v. The compositions of the solutions used for determining IECs are summarized in Table S8 (see Appendix). Eu, Gd, Y and Hf were not studied as their concentrations (below 50 ng L^{-1}) were too low to skew the determination of PGEs using the ICP-MS method applied. The IECs are displayed in Table S9 (see Appendix).

For iridium, the IECs were likely due to the background noise of the device as it was similar whatever the interferent tested. For Rh, values obtained were more difficult to fully explain especially for AG MP-1 MLL for which Sr and Pb were the main interferents. Zn was not supposed to interfere on Rh at such a concentration according to Table S9 (see Appendix) and no contribution was expected from the hydrochloric acid as HCl blanks were below 2 pg L^{-1} .

Concentrations of PGEs found thanks to DGT samplers were calculated using Equation 4:

$$C_{PGEs\ effluent} = \frac{(C_{PGEs\ eluate} - C_{blank\ resin}) * f_{analysis} * V_{elution} * e}{D_{PGEs}(T) * t * A * f_e} \text{ (Eqn. 4)}$$

With $C_{PGEs\ effluent}$, the mean concentration of PGEs in the effluent during the exposure time ($ng\ L^{-1}$); $C_{PGEs\ eluate}$, the concentration of PGEs determined by ICP-MS ($ng\ L^{-1}$) and corrected from IECs; $C_{blank\ resin}$, the concentration of PGEs initially present in the resin or the eluting solution ($ng\ L^{-1}$); $f_{analysis}$, the factor of dilution used for the analysis; $V_{elution}$, the volume of the elution solution and the gel (cm^3); e , the thickness of the diffusive gel and the filter (cm); $D_{PGEs}(T)$, the diffusion coefficient ($cm^2\ s^{-1}$) presented in section 3.2.1 adjusted with the Stokes-Einstein (Eqn. 2 and 3) law to take into account the temperature (corresponding to T, in Kelvin, under brackets) of the outflow; t , the time of exposure (s); A , the area exposed (cm^2); f_e , the elution factor proposed in section 3.1.2.

The final concentrations, determined using DGT samplers, are summarized in Table 7. Information on eluate values (blank samples and resins exposed 2 weeks in MLL and VDA WWTPs) are available in Table S10 (see Appendix).

Table 7: Concentrations of PGEs determined with DGT samplers ($n = 3$, values in $pg\ L^{-1}$).

	AG MP-1 VA	AG MP-1 MLL	S-920 VA	S-920 MLL
Ru	24 ± 4	14 ± 9	17 ± 7	N.Q.
Rh	4.2 ± 0.8	8 ± 1	N.Q.	N.Q.
Pd	N.D.	N.D.	N.Q.	69 ± 48
Ir	8 ± 2	7 ± 7	N.D.	N.D.
Pt	490 ± 20	2,300 ± 10	614 ± 156	2,251 ± 106

N.D. stands for not determined due low adsorption of Pd on AG MP-1 and the weak elution of Ir for S-920 (see respectively section 3.1.2 subsection selection of resins and elution). N.Q. stands for not quantifiable due to values close to the blank samples. Uncertainties represent the standard deviation of the replicates.

Apart from concentrations of platinum which were determined in both effluents, the results obtained for S-920 were generally difficult to interpret because the concentrations in the samples

were close to the blank values or showed high standard deviations between the triplicates. Concentrations of Ru and Pd were also determined, respectively for VA and MLL WWTPs. Concerning AG MP-1, Ru, Rh, Ir and Pt were systematically determined for both WWTPs.

Based on the determination of IECs, it appears that AG MP-1 is more appropriate than S-920, especially for Rh, which can be impacted mainly by Pb and Sr. Zn and Cu are also possible interferents but not relevant in this study due to their relatively low concentrations. Moreover, the blank values seem to be highly related to thiourea amount in solution. Blank values are comparable for both resins because S-920 elution used twice more thiourea than for AG MP-1 but the dilution is also twice more important. Consequently, the limit of detection for PGEs related to the S-920 resin is twice more important.

Generally, DGT concentrations were far below those recorded by discrete samplings. This difference could be explained both (i) by the removal of some residual spectral interferences (on Pd and Rh) and (ii) by taking into account of the labile fraction only. Concentrations of PGEs ranged from 4 $\mu\text{g L}^{-1}$ to 2.3 ng L^{-1} with maximal concentrations found for platinum due to the presence of platinum-based drugs. When results could be compared between the two resins, the concentrations obtained were in good agreement (*e.g.* Pt). This was surprising since the diffusion coefficients determined for Pt drugs were found to be significantly different depending on the resin and the drug studied. Pt-drugs may be almost completely turned into labile species due to biological degradation in the human body and during the water treatment process (activated sludge). Overall, the labile fraction of Pt ranged between 15 to 20% in this study.

Taking into account that Pt was likely present as cancerostatic drugs or their derivatives, we were interested in determining the values obtained by using platinum-based drug diffusion coefficients. Considering Table S10 (see Appendix) and Equation 4, concentrations ranged from 6 to 9 ng L^{-1} for AG MP-1 and from 0.5 to 4.5 ng L^{-1} for S-920 at VA WWTP. They ranged from 28 to 44 ng L^{-1} for AG MP-1 and from 3 to 14 for S-920 at MLL WWTP. Overestimation of DGT concentrations compared with the

total concentrations were observed whatever the diffusion coefficients of the platinum-drug based used for AG MP-1 (from 2 to 4 times higher). For S-920, the results were close to the total concentrations, especially by using the diffusion coefficients of carboplatin or cisplatin.

For Rh and Pd, the total concentrations estimated in Table 6-were much higher than those obtained with passive samplers (from 2% of lability for Rh in VA WWTP to 7% of lability for Pd in MLL WWTP). If it is probable that these elements are scarcely labile in WWTPs effluents, one cannot exclude at these so low concentrations the existence of residual spectroscopic interferences that overestimates the total concentrations. Cross-calibrations with other analytical techniques and/or the use of SPE pre-concentration may tackle this issue.

Conclusion

A new resin (AG MP-1) has been proposed for the determination of Ru, Rh, Ir and Pt using DGT technique. Its performances have been thoroughly compared with those of the S-920 resin already described by Abdulbur-Alfakhoury *et al.* [30], and further studied here. Our results obtained for the S-920 resin (*i.e.* adsorption kinetics, selectivity with respect to interferents, diffusion coefficients, etc.) were in quite good agreement with those reported although a different protocol of elution was applied. For the AG MP-1 resin, the results initially seemed less promising (*i.e.* lower adsorption kinetics, less efficient adsorption and more sensitive to the variation of the pHs and or the concentration of chloride ions) after the optimization of the whole procedure. However, the specificity of AG MP-1 for PGEs accumulation and the mild elution conditions compared to the S-920 resin were two important points justifying testing the resin under environmental conditions.

Overall, this study is the first one reported about the quantification of PGEs by DGT directly in WWTPs outflow effluents and this *in-situ* monitoring technique appears promising for further development in rivers. Using the S-920 resin, the environmental study provided results for Pd, Pt and Ru. The AG MP-1 resin was more efficient for the determination of Ir, Rh and Ru. Indeed, after two weeks of exposure, even if a slight preconcentration could be observed for the S-920 resins, blank

values were generally too close from the values of the samplers deployed *in situ*. Moreover, in polluted environments with high concentrations of Pb or Zn resulting in spectral interferences during ICP-MS analyses, the AG MP-1 resin should be preferred to the S-920 resin due to lower adsorption of these elements. For the quantification of Pt, both resins were efficient and provided similar results. It has also been shown that only 15 to 20% of platinum seems labile in the WWTPs outflows by using diffusion coefficients of (hydroxy)chlorocomplexes. Finally, we have demonstrated that DGT samplers allow to determine concentrations of PGEs down to pg L⁻¹ range.

This paper also underlines an important issue on the choice of diffusion coefficients used to quantify platinum. For the first time, platinum-based drugs diffusion coefficients have been determined and the results show high differences for the two resins according to the drug in solution: the values range from $0.25 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for carboplatin with the AG MP-1 resin to $4.1 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for oxaliplatin with the S-920 resin. These data are a first step toward a better understanding of such drugs behavior in the aquatic environment. Comparisons with other analytical techniques like the voltammetry or direct bioaccumulation tests on caged organisms (*e.g. Gammarus*) should be of great interest to better understand the speciation and fate of PGEs in aquatic environments.

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Graphical abstract

