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Importance of Anthropogenic Metals in Hospital and Urban Wastewater: Its Significance for the Environment

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Abstract Thirty-four metals were analyzed by ICP-MS. Among these elements, anthropogenic silver, gadolinium and platinum, were representative markers of medical activities in hospital and urban wastewater. On working days, median hospital wastewater concentrations for anthropogenic silver, gadolinium, and platinum were approximately three, 13 and 27 times higher respectively than the Municipal wastewater. A drastic reduction of their emission was observed during non-working days (minus 94 % for gadolinium and 87 % for platinum). A large percentage of these metals are not trapped in the Treatment Plant, i.e. 88 % for gadolinium and 69 % for platinum. More than 4 kg and 350 g for gadolinium and platinum are respectively discharged per year in the River Seine. Therefore, it is imperative to eliminate these elements in the Plant.

Keywords Wastewater · Anthropogenic metals · ICP-MS

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A hundred thousand tons of drugs and metals are used throughout the world each year after human or veterinary medical prescription. Most of these substances and/or metabolites present in waste are released into the environment, with minor or no treatment at the source. Surface water and groundwater contamination by various substances, especially drugs, is well established, and has been demonstrated by numerous studies (Fatta-Kassinos et al. 2011; Escher et al. 2011) Although the environmental impact is a reality, risk assessment evaluation is difficult and the human health effect is still poorly known (Escher et al. 2011). Therefore, environmental pollution remains a topic of major concern for citizens and public authorities.

Drugs and metals from urine and faeces of patients are eventually discharged directly into the Hospital wastewater. To assess the environment impact of human medical treatment or diagnostic activity, we evaluated the concentration not only of metals but also pharmaceuticals commonly present in different wastewaters. In this paper based on a research program supported by grants from the Regional Heath Department of Upper-Normandy – France, the main detrimental metal results are presented. Representative samples of wastewater from Rouen University Hospital (2,500 beds) and from Rouen Treatment Plant were analyzed. Hospital wastewater (HWW) is, in fact, discharged without any treatment into the initial Municipal network wastewater of the City (an urban area of 400,000 inhabitants). The aim of this study was to particularly focus on increased concentrations of anthropogenic silver (Ag), gadolinium (Gd) and platinum (Pt) in wastewater, among 34 measured mineral elements. These three elements were also chosen not only as they have known medical application in various areas: Ag for film used in radiology, Gd as a contrast agent for Magnetic Resonance Imaging (MRI), and Pt in drug antineoplastic therapy, but also due to the

particular toxicity of Gd and Pt. The objective was to quantify the part of the hospital wastewater that contributes to urban pollution. All samples analyzed were continuous flow collections to assess the amount of Ag, Gd, and Pt present at each stage of the process from Rouen University Hospital and from the Treatment Plant. As our team is experienced in ICP-MS analysis, we were approached to conduct an in depth study regarding metals in wastewater (Goullé et al. 2005, 2009b; Guerbet et al. 2007; Saussereau et al. 2008; Lambert et al. 2010; Echaniz-Laguna et al. 2012).

Materials and Methods

During 29 days, four wastewater collections were performed each day, with samplers connected to the flow. These samples were all proportional continuous samples. The part of the flow collected was exactly three parts per 1,000, therefore the samples collected each day were entirely representative for the 24 h period at each site: hospital outlet (HWW); Treatment Plant (TPWW): inlet part, to assess the dilution effect of HWW at the entrance of the plant; middle part, after primary physicochemical treatment; outlet part, after the secondary biological treatment and just prior to water discharge into the environment i.e. the River Seine.

The HWW was not affected by rainfall events, as this water was collected separately; it was mainly tap water and patient excreta. In contrast, variations of the treatment plant flow were observed during rainfalls as rain water was also collected together with all the wastewater entering the treatment plant. The hydraulic residence duration in the Treatment Plant was 27 h, so we considered retention offset of 1 day between TPWW inlet and TPWW outlet for our statistics. During the 29 day period, 19 were working days, 10 were non-working days i.e. four Saturdays, four Sundays, plus two non-working days.

A Thermo Elemental X7CCT bench top series ICP-MS using PlasmaLab® software and equipped with a dynamic reaction cell (Thermo Optek®, Courtaboeuf, France) was used for multi-elementary determinations. ICP-MS instrumental parameters and the reagents have been previously described (Goullé et al. 2005).

All the collected wastewaters were centrifuged (10 min, $3000 \times g$) and filtered (filter 0.7 µm; Millipore®, Molsheim, France) before analysis with a validated method (Goullé et al. 2005). The wastewater samples and the reference materials were diluted in a buffer solution (1:10). For the 34 elements, after a recovery study had been conducted, a direct comparison to an external calibration curve was used. The following oxide polyatomic interferences were checked for the three elements of particular interest for ^{107}Ag: ^{16}O plus ^{91}Zr and ^{18}O plus ^{89}Y; for ^{157}Gd: ^{16}O plus ^{141}Pr and for ^{195}Pt: ^{16}O plus ^{179} H. The statistical analysis of the data was performed with the R language and environment for statistical computing (http://www.R-project.org).

Results and Discussion

As previously mentioned, a very important consideration, the part of the water collected was at the four sites exactly three parts per 1,000 of the total flow, therefore all the samples were entirely representative of the flow at the site they were obtained. The raw wastewater after centrifugation, filtration and acidic dilution is a matrix very similar to urine. Isobaric, double charged and polyatomic interferences were negligible. Furthermore, the percentage of recovery for Ag, Gd and Pt was higher than 98%. Regarding the results on reference materials, all the Z scores obtained were excellent, for the three elements mentioned ($Z < 2.0$). An external aqueous calibration curve was used that produces exactly the same results as a standard addition curve (Goullé et al. 2005). For each metal, the limit of detection (LOD) and the limit of quantification (LOQ) were measured: ^{107} Ag = 0.17 and 0.58 µg/L, ^{157} Gd = 0.001 and 0.004 µg/L, ^{195} Pt = 0.003 and 0.01 µg/L respectively.

The main results are reported Table 1. Silver concentration in the control tap water was below the LOD of 0.17 µg/L. The 29 days HWW Ag median concentration was 2.9 times higher than the TPWW inlet. Metal was eliminated during the treatment plant process, and was not detectable in the middle or the outlet part of the TPWW. Silver daily median HWW concentrations were below the LOD on Saturday, Sunday and non-working days. The two highest concentrations (up to 10.00 ± 0.50 µg/L) were observed on two Mondays following two series of three non-working days, and one non-working day following two series of three non-working days, one non-working day followed by a week-end (Fig. 1). During the 19 working day period, the HWW Ag median concentration (2.65 ± 0.13 µg/L) was also 2.9 times higher than the inlet part of the TPWW (0.90 ± 0.05 µg/L) which was significantly different ($p = 1.0 \times 10^{-5}$, Student's t test). Silver was not detectable either in the HWW or in the inlet part of the TPWW during the 10 non-working days.

Gadolinium concentration in the control tap water was below the LOD of 0.001 µg/L. The median concentrations in the four wastewaters (HWW, inlet, middle and outlet parts of the TPWW) were consistent with the fact that the HWW median anthropogenic Gd concentration was approximately 12 times higher than the inlet part of the TPWW. Mean anthropogenic Gd per day was

Table 1 ICP-MS metals concentration in hospital and treatment plant wastewater

Element	LOD	Tap water	Period	Median concentrations (SD) (μg L^{-1})			
				HWW	TPWW inlet part	TPWW middle part	TPWW outlet part
^{107}Ag	0.17	<LOD	Total (n = 29)	1.87 (0.17)	0.65 (0.17)	<LOD	<LOD
			WD (n = 19)	2.65 (0.17)	0.90 (0.17)	<LOD	<LOD
			NWD (n = 10)	<LOD	<LOD	<LOD	<LOD
^{157}Gd	0.001	<LOD	Total (n = 29)	2.44 (0.12)	0.21 (0.01)	0.19 (0.01)	0.17 (0.01)
			WD (n = 19)	3.25 (0.16)	0.25 (0.01)	0.23 (0.01)	0.17 (0.01)
			NWD (n = 10)	0.21 (0.01)	0.04 (0.01)	0.06 (0.01)	0.15 (0.01)
^{195}Pt	0.003	<LOD	Total (n = 29)	0.35 (0.02)	0.02 (0.01)	0.02 (0.01)	0.01 (0.01)
			WD (n = 19)	0.61 (0.03)	0.02 (0.01)	0.02 (0.01)	0.01 (0.01)
			NWD (n = 10)	0.08 (0.01)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)

HWW hospital wastewater, *TPWW* Treatment plant wastewater, *WD* working days, *NWD* non working days, *LOD* limit of detection

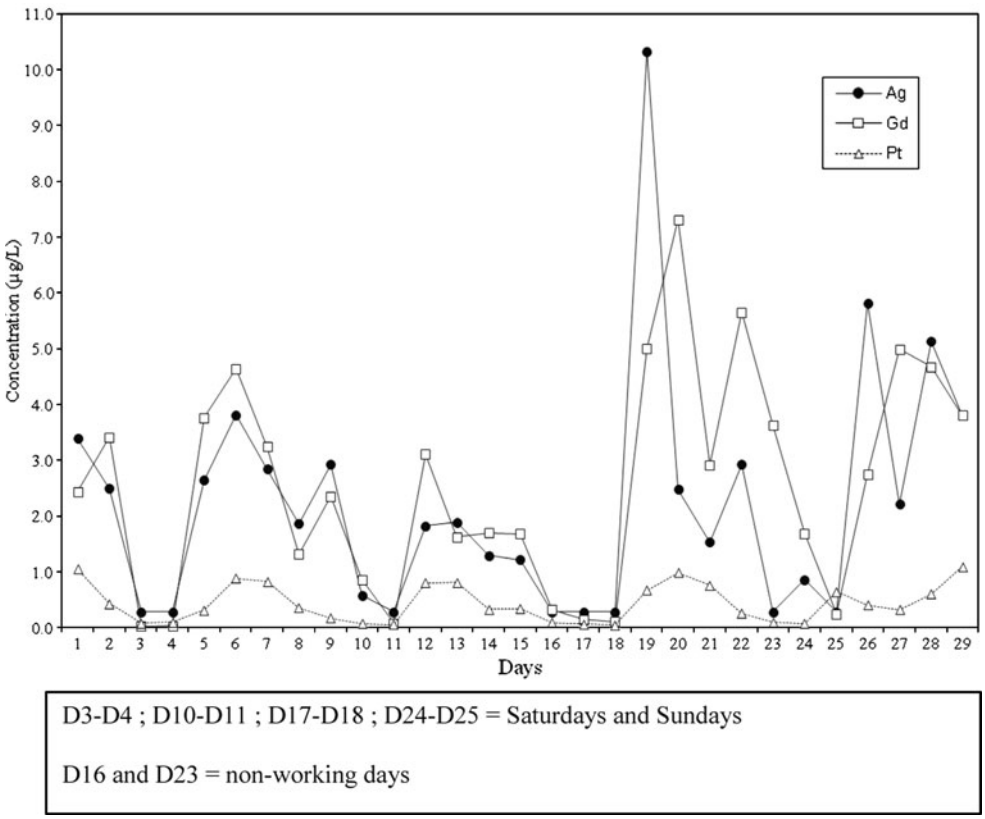

Fig. 1 Major hospital wastewater Ag, Gd and Pt concentrations decrease occurring on week-ends

13.86 ± 0.69 g, and 12.18 ± 0.61 g in the inlet and in the outlet part of TPWW respectively. The lowest HWW anthropogenic Gd concentrations were measured on Saturday, Sunday and non-working days (Fig. 1). During the 19 working day period, the HWW anthropogenic Gd median concentration (3.25 ± 0.16 μg/L) was 13 times higher than the inlet part of TPWW (0.25 ± 0.01 μg/L) over the considered period ($p = 2.0 \times 10^{-4}$, Student's *t* test). The HWW anthropogenic Gd median concentration during the 19 working days was 3.25 ± 0.16 μg/L compared to the 0.21 ± 0.01 μg/L concentration during the 10 non-working days ($p = 2.0 \times 10^{-4}$, Student's *t* test). Metal elimination was negligible i.e. only 12 % during the wastewater treatment plant process as TPWW outlet anthropogenic Gd total concentration from day 2 to day 29 was 341 ± 17 g compared to 388 ± 19 g present in the inlet part of the TPWW from day 1 to 28.

Platinum concentration in the tap water was below the LOD of 0.003 μg/L. The HWW Pt median concentration (0.35 ± 0.02 μg/L) was approximately 18 times higher than the inlet part of the TPWW (0.02 ± 0.01 μg/L). Mean Pt per day was 1.43 ± 0.07 g, and 0.99 ± 0.05 g in the

inlet and in the outlet parts of the TPWW respectively. As for Gd, the HWW Pt lowest concentrations were measured on Saturday, Sunday and non-working days (Fig. 1). During the 19 working day period, the HWW Pt median concentration (0.61 ± 0.03 μg/L) was 27 times higher than the inlet part of the TPWW (0.02 ± 0.01 μg/L) over the considered period ($p < 1.0 \times 10^{-4}$, Student's t test). The HWW Pt median concentration during the 19 working day period was 0.61 ± 0.03 μg/L, compared to the 0.08 ± 0.01 μg/L concentration during the 10 non-working days ($p < 1.1 \times 10^{-5}$, Student's t test). The metal elimination was only partial i. e. 31 % during wastewater treatment plant process as the outlet TPWW total concentration from day 2 to day 29 was 27.7 ± 1.4 g compared to 40.1 ± 2.0 g present in the inlet part of the TPWW from day 1 to day 28. Although it was possible to measure the contribution of the hospital for anthropogenic Gd and Pt, we were not able to measure Ag due to concentrations below the LOD in the outlet part of the TPWW. The hospital waste contribution in the plant for Gd and Pt was approximately 5.3 % (20.6 ± 1.0 g out of 388 ± 19 from day 1 to day 28) and 9.4 % (3.75 ± 0.19 g out of 40.1 ± 2.0 from day 1 to day 28 respectively).

Due to proportional continuous samples, strictly three parts in 1000; the samples analyzed were representative for the four sites (HWW, inlet middle and outlet parts of the TPWW) during the 24 h period. Therefore, even if there were variable concentrations in the wastewaters at different times of the day, the collected samples being proportional continuous samples were entirely representative of these variable concentrations during each 24 h period. The maximum metal concentrations measured in the HWW for anthropogenic Ag, Gd and Pt were approximately 10.0, 7 and 1 μg/L respectively. The inlet TPWW maximum concentrations were much lower, approximately 1.00, 0.30 and 0.05 μg/L respectively. Nevertheless, the median daily HWW flow concentration was only 289 m^3 per day compared to the huge TPWW inlet flow of 82,000 m^3, thus as the samples are representative, the hospital contribution to the treatment plant was only 5.3 % and 9.4 % for the Gd and the Pt respectively. Ag in hospital wastewater was mainly due to the use of this element for traditional X-ray film for mammography. Considering this activity is open exclusively during working days, Ag was detectable in HWW only on these days. During non-working days, the concentration of the element was below the LOD. During working days Ag concentration in the HWW could be used to evaluate the mammography activity levels as the element was mainly used for this radiological examination. A large part of the metal was removed during the plant process, but it was impossible to quantify as the concentrations were below the LOD in the middle and outlet sites of the TPWW during working days, and never detectable at any stage of the process during non-working days. We can therefore assume that this mineral form of Ag is trapped with particles and solids during the primary physico-chemical treatment.

The source of anthropogenic Gd in the HWW was linked with hospital MRI examinations. Gadolinium is injected into the patient's blood in the form of an organic chelate to prevent the high Gd^{3+} ion toxicity. The organic complex is then rapidly cleared from the body as the half-life is about 1.5 h (Goullé et al. 2009a). Due to this short half-life, the drug is mostly eliminated in the urine on the day of the examination and is mainly present in the HWW from Monday to Friday. Anthropogenic Gd water concentrations also decrease in the plant wastewaters during week-ends and non-working days. Hospital anthropogenic Gd contribution was 5.3 % of the total amount of metal entering the plant, but its flow was only 0.3 % of the plant entrance flow. For this reason, Gd should be considered an effective marker of MRI diagnostic radiology medical activity. Many authors have focused on water pollution due to this metal (Kümmerer 2001; Rabiet et al. 2009). As the samples were entirely representative, we could assume that probably due to the particular form of the Gd, an organic chelate, the element is moderately trapped in this form during the plant process and approximately 88 % (the TPWW outlet total TPWW outlet concentration from day 2 to day 29 was 341 ± 17 g compared to a total quantity of 388 ± 19 g present in TPWW inlet from day 1 to 28). Therefore, the anthropogenic Gd is still present in the outlet part of the plant and more than 4 kg per year are discharged into the River Seine. There it will become a conservative tracer, either mineral or organic. However, due to the accumulation, increased levels of this metal in the environment may be eventually detected in tap water (Lawrence et al. 2009).

Platinum derivatives i.e. oxiplatin, cisplatin, carboplatin, have been used for many years in cancer treatment and have been identified in hospital sewage (Kümmerer and Helmers 1997). The amount of Pt eliminated by hospitals probably represents only a small part of the Pt found in the environment (3.3 %–12.3 %), the main source constituted by releases from vehicle catalytic converters (Kümmerer et al. 1999). It is a real challenge to calculate the amount of metal released by catalytic converters and the quantity delivered by medical activity As only 31 % of the Pt were trapped in the Plant, the estimated annual quantities released into the environment via wastewater were more than 350 g for the city of Rouen, but only 9.4 % directly attributable to the Hospital. These results were markedly different from those published by Lenz et al. (2007) for whom platinum elimination during the treatment process of hospital effluents ranged between 51 % and 63 %.

In order to effectively assess all possible elements in hospital wastewater, we first analyzed a total of 34

elements. Three of them, Ag, Gd, and Pt, were particularly selected as being the most representative of wastewater contamination due to medical activities, but also because Gd and Pt are problematic due to their toxicity. For example, as previously mentioned, Ag originates from film used to perform mammography, Gd injected into patients for MRI, and Pt perfusion during antineoplastic chemotherapy. These element concentrations were significantly higher in hospital wastewater than in urban wastewater, but when compared to the respective flow of hospital and urban wastewater, the hospital contribution only ranged from 1.3 % to 9.4 % for these three elements. As the samples collected were representative of the total flow at each location due to proportional continuous samples, we were able to confirm that during the plant treatment process, Gd and Pt were poorly removed from wastewater, as approximately 88 % and 69 % respectively are discharged from the plant, into the environment, via the River Seine. As previously underlined, regarding anthropogenic Gd and Pt, in fact more than 4 kg and 350 g respectively per year accumulate in the environment. Due to their toxicity and current lack of data concerning their presence in the environment, specific treatment of wastewater for Gd and Pt must be considered. It is important to note that the impact of these substances will continue to increase owing to their basic general use, as well as ever expanding diagnostic and therapeutic applications. As the Hospital wastewater flow contribution to the total Plant flow is negligible i.e. 0.35 %, the Gd and Pt Hospital elimination part is only 5.3 % and 9.4 % of the total, therefore the specific elimination of these elements should be located directly at the Treatment Plant.

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Conflict of interest The authors declare that there are no conflicts of interest.

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