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Semi-continuous pharmaceutical and human tracer monitoring by POCIS sampling at the watershed-scale in an agricultural rural headwater river

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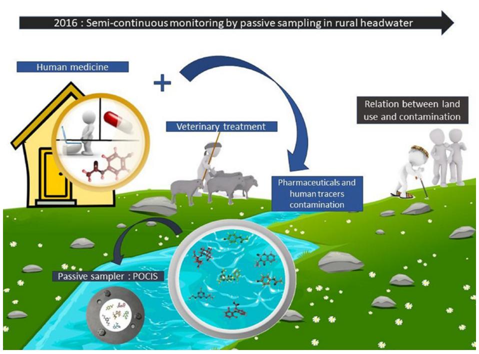
GRAPHICAL ABSTRACT



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ABSTRACT

Pharmaceutical monitoring (37 pharmaceuticals and 3 human tracers) was conducted in a headwater streams in southwest France, an area characterized by a low population density with an elderly population (30% > 60 years old) and extensive agriculture (cow cattle breeding). Polar Organic Chemical Integrative Sampler (POCIS) were exposed for 14-day consecutive periods in 2016 at three sampling points. Three human wastewater tracers and 20 pharmaceuticals commonly used for human and/or cattle were quantified in headwaters. Succession of small Wastewater Treatment Plant (WWTP), non-collective sanitation, discharges of untreated effluents as well as the river ability to dilute discharged wastewater, mainly explain the pharmaceuticals and human tracers concentrations. Pharmaceutical loads were time-dependent and were higher during cold season due to increase of pharmaceutical consumption. In contrast, better degradation and/or sorption onto river biofilms in warm season induced the decrease of headwater pharmaceutical content. The headwaters streams were contaminated by compounds found in other type of watershed, but β-blocker were the compounds quantified in higher concentration with frequencies of 100%, which was consistent with the elderly population living in the watershed. Specific compounds (sulfamerazine and sulfamethoxazole) used to cattle medical care were detected in waters, but at a low content.

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1. Introduction

The presence of pharmaceuticals, veterinary drugs and hormones in freshwater has been reported by numerous studies (*e.g.* [1–4]) but more research is required for establishing occurrence, exposure and effects [2,5]. These compounds pollute aquatic environments in various ways, but WasteWater Treatment Plants (WWTP) are the major contamination pathway [5]. Pharmaceuticals have been widely detected in waters all around the world with concentrations ranging from ng to µg/L, depending on regions and seasons [1,6–8].

Headwater streams were, for a long time, considered the less contaminated areas (for organic and inorganic compounds) because of low human pressure (*e.g.* low population density, extensive farming (*i.e.* with a low density of cow in the meadows and with limited supply of fertilizer and pesticides – see Figure S1 in supplementary material), numerous forests). This type of watershed plays a huge role in biodiversity, containing numerous species of high biological value [9]. Headwater streams are characterized by wetlands, low flow rates and rapid contaminant transfer due to the presence of numerous very small streams. Thus, small and often old, WWTP from nearby small towns can represent a significant part of the water flow and may result in pollution by pharmaceutical contaminants.

In addition to pharmaceuticals, anthropogenic markers can be monitored, such as caffeine or sucralose, which are very frequently detected in water [10]. By their high human consumption, caffeine and sucralose have been monitored as human tracers in water [10]. These compounds are found in drinks (*e.g.* coffee, tea, soft drinks), food products (*e.g.* chocolate, candies…) and also, for caffeine, in psychoactive stimulant drug. Depending on study region, other compounds can be monitored as human tracers, such as some illicit drugs (amphetamine, methamphetamine, cocaine and benzoylecgonine) [4,11] or hormones (estrone, estradiol, progesterone or derivates) [4] [12]. Nevertheless, due to the ability of WWTP to remove hormones from wastewater, only estrone was more interesting as a tracer of treated wastewater discharge in rivers [13].

Traditionally, grab sampling has been used to evaluate the presence of pharmaceuticals in aquatic environments. This technique does not perform well enough when pharmaceuticals are present at low concentration in freshwaters. Moreover, this technique presents other disadvantages such as the lack of temporal representativeness [14]. Passive samplers such as the Polar Organic Chemical Integrative Sampler (POCIS) appear to be a very interesting alternative to grab sampling [15]. POCIS continuously accumulates pharmaceuticals and allows lower quantification limits [16]. A better estimation of contamination with time-weighted averaged concentrations (TWAC) can be calculated [15,17]. From TWAC, real load of compounds can be estimated if flow rate at the sampling site is available [18]. Poulier et al., (2014) estimate TWAC uncertainty about factor 2 because of accumulation on POCIS could be influenced by environmental conditions (*e.g.* temperature, flow velocity…).

Currently, headwater plays an important role in aquatic biodiversity and river quality must be better characterized [19]. Nevertheless, this water quality, regarding for example organic micropollutants, is under-researched. To our knowledge, pharmaceutical contamination of such watersheds is poorly documented, except for Wilkinson et al. [4], who reported slight contamination downstream of a WWTP. To better specify the pharmaceutical contamination state of headwaters, a 1-year study using POCIS semi-continuous sampling was performed at the watershed-scale (Aixette watershed in south-west France). This headwaters watershed, like numerous rural headwaters watershed in France, is characterized by a low population density, an elderly population and extensive agricultural activities (mainly cattle breeding).

2. Materials and methods

2.1. Materials and chemicals

Ultrapure water (UPW) was produced by a Gradient A10 Milli-Q system from Millipore. Organic solvents (HPLC-MS quality) were obtained from Carlo Erba for methanol (MeOH), Sigma Aldrich for ethyl acetate, J.T. Baker for formic acid and Scharlau for ammonium formate. The list of pharmaceuticals (37 compounds) and human tracers (3 compounds – caffeine, sucralose and a caffeine metabolite: paraxanthine) with purity, CAS number and chemical formula is presented in supplementary materials (Table S1). Action classes and use of the studied pharmaceuticals and human tracers are presented in Table S2 (16 compounds were only used for humans, 3 were only used for animals and 20 were common to human and animals). Compounds were purchased from HPC Standards GmbH (16), Ehrenstorfer GmbH (10), Sigma-Aldrich (8), Dr. Santa Cruz Biotechnology (5), or Neochema (1) with a purity ≥ 91.7% (Table S1). Stock pharmaceutical solutions at concentrations of 100 mg/L were prepared in MeOH and stored at −18 °C. A working solution containing all compounds was prepared at 1 mg/L in MeOH with a dilution of stock solutions and stored at −18 °C for no more than 6 months.

Internal standards are presented in supplementary materials Table S3. Internal standard solutions were prepared in MeOH at 10 mg/L and stored at −18 °C. Fresh calibration solutions containing pharmaceutical standards (1, 2, 5, 10, 25, 50 and 100 µg/L) and internal standards (100 µg/L) were prepared before analysis in a mixture of UPW:MeOH (90:10 v:v).

2.2. Main characteristics of the headwater

The study was done on one headwater streams located in southwest France (Haute-Vienne, Nouvelle Aquitaine): the Aixette watershed. The Aixette watershed localization and sampling point is presented in supplementary material (Figure S2). The climate is characterized as degraded Atlantic oceanic (continental influence) with mild and wet seasons. Three sampling points were chosen: two on the Aixette River (Aixette Upstream and Downstream) and another on a tributary of the Aixette River, the Arthonnet. The first sampling point (Aixette Upstream) was located 13.5 km from the spring at Lavignac, the second (Aixette Downstream) was located 5 km before the confluence with the Vienne River and 8.4 km after the Aixette Upstream sampling point. The last point (Arthonnet) was located before the outlet of the tributary' "The Arthonnet" which meets the Aixette between the first two sample points at Pont Péry. The size of the watershed is 163 km^2. The end of the Aixette watershed is in a peri-urban area of the city of Limoges. The 3 sampling points were located in the rural agricultural part of the Aixette watershed where agricultural lands were composed of grassland (37%) with extensive cattle breeding (a picture of extensive agriculture are shown in Figure S1), cultures (37%), forest (16%), arable land (3%) and urban area (3%) (see Aixette watershed land-use in supplementary material Figure S2). In this extensive agriculture watershed, the density of cow is 280 and 210 cow/km^2 for Arthonnet and Aixette watershed, respectively.

The population density is low (from 23.2–63.6 inhabitants/km^2 in the main municipalities of the watershed, the average in France is 118 inhabitant/km^2, Table S4). The population distribution in Haute-Vienne (French department where headwaters watershed of Aixette is located) in 2016 was: 22% [0–19 years old], 22% [20–39 years old]; 26% [40–59 years old]; 18% [60–74 years old]; 12% [> 75 years old] [20]. The population density is low with 30% of the population are over 60, which is significantly more than the French average (25% > 60 years old). Six small WWTP are located in the Aixette watershed and are presented in Figure S2. Two WWTP are before the Aixette Upstream sampling point: 1350 population equivalent (PE – definition in supplementary material) and 217 PE. One WWTP of 367 PE is before the