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The impact of a Wastewater Treatment Works in Southern Gauteng, South Africa on efavirenz and nevirapine discharges into the aquatic environment

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ABSTRACT

There has been growing concern regarding the pollution of the aquatic environment with synthetic organic chemicals. Antiretroviral drugs, such as efavirenz and nevirapine, are pharmaceutical drugs and are referred to as emerging contaminants. Such drugs can be environmentally persistent and may be expected to pose potential risks to drinking water supplies.

Sources of pharmaceutical drugs include effluents from Wastewater Treatment Works (WWTPs), hospital and pharmaceutical production facilities and the incorrect disposal of unused and expired medicines. Currently there are no monitoring programs and legislative guidelines for their regulations in South Africa.

The aims of this study were firstly to develop a semi-quantitative method to extract and analyse efavirenz and nevirapine in the primary settling tank sludge. Secondly to use that method, and an existing method for liquid wastewater samples, to monitor the concentrations of efavirenz and nevirapine as the wastewater passes through the different stages of purification (anoxic; aerobic; pre and post chlorination) in the WWTP. This was repeated weekly over a period of 4 weeks. Thirdly, to determine if binding of efavirenz and nevirapine to the solids in the WWTP played a role in the removal of these compounds from the WWTP liquid phase. No references to the analysis of ARVDs in WWTP sludge were found in the literature.

Grab samples of wastewater and sludge samples were collected from a WWTP (activated sludge treatment process) weekly for 4 weeks. Liquid samples were extracted solid phase extraction, solid samples were extracted using sonication followed by a QuEChERs clean-up. Sample extracts were then subjected to gas chromatography-time of flight mass spectrometry for analyte determination.

Efavirenz concentrations entering the WWTP ranged between 5500 to almost 14 000 ng/L. The removal of efavirenz by the WWTP ranged between 27 and 71%. The largest removal occurred in the anoxic zone, smaller amounts were removed in the aerators. Slight increases in efavirenz concentrations were found after chlorination and the final effluent into the river post maturation ponds again were slightly lower. Solids were found to contain efavirenz at concentrations between 17 and 43 mg/kg dried primary settling tank sludge and it is proposed that this binding to the solids is the main mechanism of removal of efavirenz from the wastewater stream as it passes through the WWTP.

Although an order of magnitude lower nevirapine concentrations displayed the opposite behaviour and gradually increased through the various stages of purification in the WWTP. Minor fluctuations occurred but the concentrations of nevirapine were higher at the effluent (between 92 and 473 ng/L) than those entering the WWTP. No nevirapine was detected in the PST sludge. The increase in nevirapine concentrations are likely to be the result of the de-conjugation of the hydroxylated metabolites of nevirapine in the WWTP, its resistance to degradation and the lack of binding of the nevirapine to the PST sludge.

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1. Introduction

There has been growing concern regarding the pollution of the aquatic environment with synthetic organic chemicals. Some of the synthetic organic chemicals include, but are not limited to, Pharmaceutical and Personal Care Products (PPCPs). A number of these are known to be persistent, bio-active and bio-accumulative and display endocrine disrupting activities [1]. Pharmaceutical drugs include non-steroidal drugs such as analgesics, antibiotics, anti-epileptics, b-blockers, blood-lipid regulators and antiretroviral drugs (ARVDs) and steroidal drugs (hormones). Other endocrine disrupting compounds (EDCs) such as drug additives are also of concern.

The impacts of EDCs that are more environmentally persistent can be expected to pose greater potential risks to drinking water supplies. Pharmaceutical compounds were not thought to pose a significant risk to human health via drinking water and the consumption of fish [2], however, a study on the impact of a Wastewater Treatment Works (WWTP) in Spain showed that PPCPs, rather than the traditional priority pollutants, contributed to water toxicity [3]. The parent compounds, as well as their degradation products, can be expected to play a role in this toxicological impact. Sources of pharmaceutical drugs include effluents from WWTPs [4,5], hospital and pharmaceutical production facilities [6] and the incorrect disposal of unused and expired medicines [7]. A survey conducted in the United States showed that these drugs generally either end up in solid waste landfill sites or WWTPs [7].

The World Health Organisation estimated in 2012 that 2 500 000 people in South Africa required antiretroviral therapy [8]. Recent estimates indicate that as many as 7 million people may be infected with HIV and of those, half are on ARVDs [9]. A daily dose of combination therapy of ARVDs (mean of 991 mg/day/person, range 590–1996) equates to a total of 1.27 million kg of ARVD compounds ingested per year (assuming 3.5 million people are on ARVDs). Excretion of ARVDs varies depending on compound, as tipranavir is excreted at 80% and nevirapine at 2.7% via urine [10]. Assuming a mean of 30% excretion to sewage via urine and faeces, it is estimated that almost 380 000 kg of ARVDs could reach the aquatic systems of South Africa every year [10]. The most common combination HIV-ARVs used for first line treatment for HIV affected adolescents, adults and pregnant woman is a cocktail made up of efavirenz, tenofovir and emtricitabine (or lamivudine). Efavirenz may be replaced with nevirapine in the case of psychiatric co-morbidity or intolerance to efavirenz [11]. Efavirenz and nevirapine (both non-nucleoside reverse transcriptase inhibitors) are thus likely to be detected in WWTP influents.

WWTPs are designed to remove solids, dissolved organic matter and nutrients from wastewater [12]. Activated sludge processes are still widely used in WWTPs (and is utilized in the WWTP that is the subject of this study) because they produce effluents that meet required quality standards at reasonable operating costs [13] but were never designed to remove pharmaceuticals and often do not eliminate them efficiently [14,15]. Many of the pharmaceutical compounds are highly water soluble and resistant to biodegradation. This results in their incomplete elimination in the WWTPs [16].

The removal of pharmaceuticals in a WWTP occurs via microbial biodegradation [17] and/or adsorption to sludge [18]. Advanced oxidation processes, such as ozonation, have been found to reduce amounts of pharmaceuticals leaving WWTPs [19]. These are costly processes and more likely to be found in WWTPs in developed countries.

In a study in Greece it was reported that the rates of removal of pharmaceuticals varied greatly [20]. Removal efficiencies of the analytes varied from relatively high (salicylic acid and ibuprofen) to medium (sulfamethoxazole and fenofibrate) to low (trimethoprim). Some displayed negative removal efficiencies (carbamazepine and diclofenac). Eight WWTPs were investigated, all using conventional activated sludge treatment.

A study on the ability of 4 WWTPs in Kenya to remove pharmaceuticals was reported on by Jebiwot [21]. All of the WWTPs made use of wastewater stabilization ponds (WSPs), one WWTP included trickling filters and another included an anaerobic pond, details shown in Table 1.

On average, WWTP 3 recorded a slightly better removal efficiency (97%) than WWTP 1 (75%), WWTP 2 (82%) and WWTP 4 (86%). Of all of the pharmaceuticals monitored only carbamazepine (0 - 90%) and nevirapine (6 - 84%), showed to be relatively persistent in the WWTPs. In some instances nevirapine increases were observed in the anaerobic pond and this was attributed to de-conjugation of the hydroxylated metabolites of nevirapine. Similar removal efficiencies were observed in WWTP 2 and WWTP 3. Efavirenz removal efficiencies were excellent (>80%).

K'oreje observed similar results in another study in Kenya [22] where nevirapine concentrations as high as 1–2 μg/L were reported and removal efficiencies of between 11 and 49% were observed. Similar low removal efficiencies of nevirapine is reported by Prasse in activated sludge WWTPs.

Wood reported on a study that investigated the chlorination behaviour of nevirapine [23] where it was established that the drug was resistant to degradation at relevant chlorination levels. Disinfection transformational products were however formed during simulated chlorination, these compounds were also detected in in the environment, close to WWTPs.

The low concentrations of pharmaceutical drugs that can be present in environmental waters necessitates the pre-concentration of the analytes prior to analysis.

The most common method of extraction is Solid Phase Extraction (SPE). With SPE, analytes are partitioned between a liquid and a solid sorbent phase and must have a greater affinity for the sorbent facilitating their extraction from the liquid phase [24]. Solid-phase Microextraction (SPME) is an extraction technique that is similar to SPE but uses a much lower volume of sorbent [24]. The sorbent in this case is a polymeric stationary phase that is attached to a short length of fused silica that is in turn fixed to a stainless steel needle.

The high polarity of many pharmaceuticals means that liquid chromatography (LC) is the best method to analyse extracts containing these compounds. The most suitable detector for these compounds is mass spectrometry. Only mass spectrometry is sufficiently sensitive and selective to determine the pharmaceutical compounds at very low concentrations and in the complex matrices encountered [25]. High resolution (accurate mass) mass spectrometry instruments are able to be run in full scan mode and thus overcome the limitations of target type analyses and include time-of-flight [26] and magnetic sector instruments LC methods are commonly used for determining efavirenz and nevirapine. Detection is by UV, fluorescence, MS and MS/MS and allows quantification, either individually or simultaneously in biological matrices [27]. The determination of ARVDs in South African waters using MS/MS is described [28] and in wastewater and surface water

Table 1
WWTP location and treatment processes.

WWTP	Location	Purification Process
1	Eldoret	WSPs, Trickling filters
2	Kitale	WSPs
3	Mumias	WSPs
4	Kakamega	WSPs, Anaerobic pond