Chemosphere 168 (2017) 1042–1050

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Detection and quantification of acidic drug residues in South African surface water using gas chromatography-mass spectrometry

Bhekumuzi P. Gumbi [a], Brenda Moodley [a], Grace Birungi [b], Patrick G. Ndungu [c, *]

[a] University of KwaZulu-Natal, School of Chemistry and Physics, Private Bag x 54001, Durban 4000, South Africa
[b] Mbarara University of Science and Technology, Department of Chemistry, Private Bag 1410, Mbarara, Uganda
[c] University of Johannesburg, Department of Applied Chemistry, Doornfotein, Private Bag 17011, Johannesburg 2028, South Africa

HIGHLIGHTS

- Quick easy method for moderately equipped labs in middle income countries.
- Acidic drugs can be detected and quantified in surface and waste water samples.
- Occurrence of acidic drugs in environmental samples in Southern Africa.

ARTICLE INFO

Article history:
Received 13 July 2016
Received in revised form
24 October 2016
Accepted 26 October 2016
Available online 1 November 2016

Handling Editor: Klaus Kümmerer

Keywords:
Acidic drugs
Method validation
Derivatization
GC-MS
Surface water
Umgeni river

ABSTRACT

A method was optimized for derivatization, separation, detection and quantification of salicylic acid, acetylsalicylic acid, nalidixic acid, ibuprofen, phenacetin, naproxen, ketoprofen, meclofenamic acid and diclofenac in surface water using gas chromatography-mass spectrometry. For most of the acidic drugs, recovery was in the range 60–110% and the percent standard deviation was below 15% for the entire method, with limits of detection ranging from 0.041 to 1.614 μg L^{-1}. The developed method was applied in the analysis of acidic drugs in Umgeni River system, KwaZulu-Natal South Africa. All of the selected acidic drugs were detected and quantified, their concentration in Umgeni River system ranged from 0.0200 to 68.14 μg L^{-1}.

1. Introduction

In recent years, pharmaceutical compounds have been reported to be present in wastewater effluent, drinking water, rivers and dams in Asia (Saravanan et al., 2014; Shanmugam et al., 2014; Chen et al., 2015; Jindal et al., 2015; Li et al., 2015; Qin et al., 2015), America (Sarmah et al., 2006; Kümmerer, 2009; Caracciolo et al., 2015; Qin et al., 2015), Australia (Sarmah et al., 2006; Watkinson et al., 2009) and Europe (Sarmah et al., 2006; Kümmerer, 2009; Valcárcel et al., 2013; Frederic and Yves, 2014; Net et al., 2015). However, within Africa, there is limited information concerning the occurrence of pharmaceuticals in the environment (Agunbiade and Moodley, 2014; Madikizela et al., 2014; Shanmugam et al., 2014; Matongo et al., 2015). In part, due to the lack of suitable methods that can be used with the limited analytical facilities available.

Pharmaceuticals play an important role in safeguarding people's health (Hotez and Kamath, 2009). However, some, like acidic drugs do not completely degrade in wastewater water treatment plant processes (Lacey et al., 2012), and their presence in the environment can be hazardous towards humans, terrestrial and aquatic organisms, and can disrupt ecosystems (Celiz et al., 2009). For example, Lacey et al. (2012) reported that diclofenac caused vitellogamin in male Japanese medaka fish, and Diniz et al. (2015) reported on the toxicity of pharmaceuticals to zebrafish. Furthermore, some drugs have been found to inhibit seed germination, and crop growth (Caracciolo et al., 2015).

Analytical methods for the quantification and monitoring of

* Corresponding author.
E-mail address: pndungu@uj.ac.za (P.G. Ndungu).

http://dx.doi.org/10.1016/j.chemosphere.2016.10.105
0045-6535/

pharmaceutical compounds, so as to elucidate their fate and behaviour within the environment are relatively complicated, time consuming and expensive (Iglesias et al., 2012). This is more so in developing countries where state of the art equipment is limited; yet routine analysis of pharmaceuticals at ng L^{-1} levels is of paramount importance (Rozet et al., 2007; Ji et al., 2014; Qiu et al., 2016). Liquid chromatography-mass spectrometry (LC-MS) and gas chromatography (GC-MS) are widely used for environmental analysis of pharmaceuticals (Petrović et al., 2005; Maggioni et al., 2013; Zhao et al., 2014; Cheng et al., 2015). LC-MS is preferred for analysis of polar, non-volatile and acidic analytes, but it can be expensive when used for routine analysis and few organisations can afford such instruments (Kumirska et al., 2015). In contrast, GC-MS is sensitive, selective, cheaper to maintain and is more readily available. Furthermore, GC-MS may be superior to LC-MS for trace analysis of organic compound in matrices of greater complexity, but is limited for non-volatile compounds in aqueous matrices (Hao et al., 2007). Derivatization methods are often used to increase volatility, reduce polarity and enhance detectability of acidic drugs by GC-MS (Lin et al., 2008). The choice of derivatizing reagents is crucial, and more so when developing a routine analytical method (Kumirska et al., 2013).

This work presents optimized methods for the quantification of acidic drugs in water samples using GC-MS. The method developed reduces the retention times 2–3 fold compared to other published methods (Togola and Budzinski, 2007, 2008; Samaras et al., 2010, 2011; Giandomenico et al., 2011; Migowska et al., 2012; Kumirska et al., 2013). In addition, a silylation derivatization was optimized to improve the GC-MS method's application to analysis of acidic drugs in South African waters.

2. Experimental

2.1. Chemicals and reagents

Aspirin, salicylic acid, nalidixic acid, ketoprofen, Ibuprofen, diclofenac, meclofenac, phenacetin, naproxen, 4,4-Di-*tert*-butylbiphenyl, dichlorodimethylsilane, 99% N,O-Bis(trimethylsilyl) trifluoroacetamide (BSTFA) and trimethylsilyl chloride (TMSC) were of analytical purity and were purchased from Sigma-Aldrich (South Africa). Cinnamic acid was purchased from BDH chemical Ltd (South Africa). Analytical grade hydrochloric acid (HCl, 37%) was bought from Merck (South Africa). Acetone, acetonitrile, dichloromethane, toluene methanol and ethyl acetate were chromasolv® grade (99.9%) purchased from Sigma-Aldrich (South Africa). Double distilled water was obtained using an Aquation Biby A4000D water purification system (Biby Sterlin LTD (UK)). All carrier gases, including those used for extraction, were of high purity (99.999%) and were purchased from Afrox (Durban, South Africa). All chemicals were used without further purification.

2.2. Apparatus, materials, and instruments

All glassware, including amber bottles used for sampling, were washed with phosphate free soap dynachem (South Africa) and soaked in an acid bath for 24 h. After the acid bath, all glassware's were then rinsed with 5% dichloromethylsilane in toluene and methanol respectively, and then heated at 60 °C for 12 h (except the sampling bottles). Small volumes were measured by micropette plus kit Dragon lab (China) ranging from 0.5 to 1000 μL. All glass fibre Millipore filters were bought from pall corporation (South Africa). Extraction manifold and sorbents used for extraction (oasis HLB 20 cc (1 g) LP, sepak-pak plus CN cartridge and tC18 environmental cartridge sepak-pak) were purchased through Microsep from Waters (United State of America (USA)). GC-MS used was a Shimadzu QP2010 SE equipped with auto injector (AOC-20i) and Auto sampler (AOC-20s) (South Africa, Kyoto Japan, respectively). GC was equipped with a capillary column, Crossbond 5% diphenyl/95% dimethyl polysiloxane (intercap SMS/Sil 0.25 mml. D x 30 M df = 0.25 μm) bought from Restek (USA). Both glassware and instrument were kept at laboratory temperature at 20 °C.

2.3. Preparation of stock solutions

Stock solutions of each compound, internal standard 2-chlorobenzoic acid, surrogate standard 3-phenylprop-2-enoic acid and injector standard 4,4-di-*tert*-butylbiphenyl (1000 μg L^{-1}) were prepared in methanol and stored at 4 °C. Working solution of the standards containing 10 000 μg L^{-1} of each target analyte and IS were also prepared and used in optimizing the derivatization procedure. For the corresponding calibration curves, standard solutions (10 μg L^{-1}–5000 μg L^{-1}) were prepared by diluting a working stock solution that contained all of the target compounds in the appropriate amounts of acetonitrile and stored in the dark at 4 °C. All solutions including samples were evaporated to dryness under a gentle stream of nitrogen, and subjected to derivatization and GC-MS analysis in optimal conditions from 1.5 mL vials.

2.4. Sampling

Sampling was carried out (January 2015; July 2016) along Umgeni River situated in Kwa-Zulu Natal province, South Africa. Umgeni River has a 4418 Km^2 catchment, 257 Km long, contains four large dams, and supports over 4 million people. Fig. 1 presents the locations of various sampling sites.

Samples were collected from Midmar dam (1), Albert Falls (2), Henley dams (3), influent (4) and the effluent (5) of the Darvil wastewater treatment plant (WWTP), Nagle dam (6), Inanda Dam (7, 8), inlet (9) and outlet (10) of the Northern Wastewater Treatment Works, and the joining point between wastewater discharge point and Umgeni estuary (11). Some communities and animals source water directly from both Nagle and Inanda dam (Fig. 1). All composite samples (5 × 500 mL) were collected from an area of 2 m^2, into 2.5 L amber bottles, Environmental parameters (pH, temperature, total dissolve solid, salinity, redox, dissolved oxygen and conductivity) were measured on site and samples were preserved at 4 °C. Samples were transported to the laboratory and stored in a freezer for later analysis.

2.5. Sample preparation

Samples were filtered through 0.45 μm glass fibre (Millipore) filters, and then 1 L of each sample was mixed with a solution of cinnamic acid in acetonitrile, as a surrogate standard (final concentration 100 ng L^{-1}), and then acidified to pH ≤ 2 with HCl. Target analytes were extracted using oasis HLB SPE cartridges. Cartridges were conditioned with 8 mL methanol and then 10 mL of distilled water (pH ≤ 2) at flow rates of 3–6 mL min^{-1}. Then 1 L of water sample was passed through the cartridge at a flow rate of 6–8 mL min^{-1} for approximately 2 h. After, cartridges were left under vacuum for 30 min, and then a gentle stream of nitrogen was passed through for 5 min. Analytes were eluted with 8 mL of acetone/ethyl acetate in ratio of 1:1 and then 1 mL of acetonitrile, at a flow rate of 0.5–1 mL min^{-1}. Sample eluate was then mixed with a 10 μL solution of *o*-chlorobenzoic acid in acetonitrile (10 mg L^{-1}), and then dried under a gentle stream of nitrogen. Samples were derivatized by adding 100 μL of BSTFA and 10 μL TMSC, in a vial sealed with Teflon lined septa and held at 70 °C in a water bath for 30 min. The derivatized sample was partially dried under nitrogen and finally re-dissolved in 1 mL acetonitrile.