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Spatial analysis and source profiling of beta-agonists and sulfonamides in Langat River basin, Malaysia

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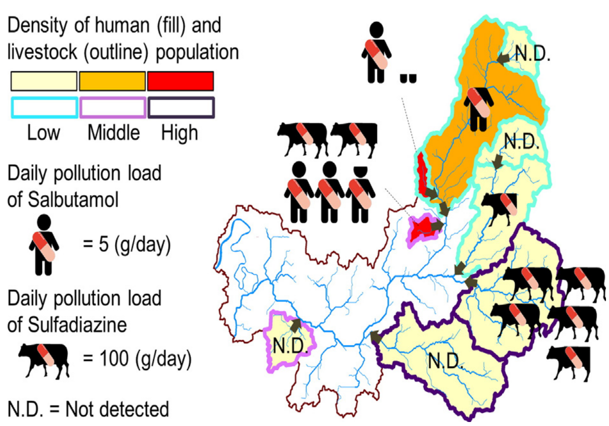
HIGHLIGHTS

- Beta-agonists and sulfonamides were quantified in the Langat River basin.
- Six compounds were widely detected in surface water especially from populated areas.
- Spatial analysis by GIS was used to estimate population density.
- Source profiling was based on estimated population density and monitoring results.
- Source profiling identified pollution sources of three compounds.

GRAPHICAL ABSTRACT



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ABSTRACT

Beta-agonists and sulfonamides are widely used for treating both humans and livestock for bronchial and cardiac problems, infectious disease and even as growth promoters. There are concerns about their potential environmental impacts, such as producing drug resistance in bacteria. This study focused on their spatial distribution in surface water and the identification of pollution sources in the Langat River basin, which is one of the most urbanized watersheds in Malaysia. Fourteen beta-agonists and 12 sulfonamides were quantitatively analyzed by liquid chromatography–tandem mass spectrometry (LC–MS/MS). A geographic information system (GIS) was used to visualize catchment areas of the sampling points, and source profiling was conducted to identify the pollution sources based on a correlation between a daily pollutant load of the detected contaminant and an estimated density of human or livestock population in the catchment areas. As a result, 6 compounds (salbutamol, sulfadiazine, sulfapyridine, sulfamethazine, sulfadimethoxine and sulfamethoxazole) were widely detected in mid catchment areas towards estuary. The source profiling indicated that the pollution sources of salbutamol and sulfamethoxazole were from sewage, while sulfadiazine was from effluents of cattle, goat and sheep farms. Thus, this combination method of quantitative and spatial analysis clarified the spatial distribution of these drugs and assisted for identifying the pollution sources.

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1. Introduction

Beta-agonists and sulfonamides are among the most commonly used veterinary drugs worldwide. Beta-agonists are used to treat cardiogenic shock, acute heart failure, bradyarrhythmias, asthma and chronic obstructive pulmonary disease (Yu et al., 2011), and also to feed them as a growth promoter in livestock feed for considerable muscle mass increase while decreasing fat accumulation (Mersmann, 1998). Similarly, sulfonamides are widely used in livestock productions for their therapeutic and prophylactic properties (Malintan & Mohd, 2006) as well as for growth promotion (Cheong et al., 2010). Environmental pollution of these drugs is concerned and beta-agonists may lead to adverse cardiovascular events (Salpeter et al., 2004), while sulfonamides may cause drug-resistant bacteria (Huovinen et al., 1995). Furthermore, beta-agonists and sulfonamides are used to treat diseases and infections for human, and they had been detected in waste streams from wastewater treatment plants, sewage treatment plants, hospitals and drug production facilities (Yu et al., 2011). Therefore, there is the potential for contamination of the water by such a wide range of treatments for both human and livestock. In Malaysia, the potential usage of banned beta-agonists in swine farms was identified (Ponniah et al., 2004), and salbutamol was detected in effluents of sewage treatment (Al-Odaini et al., 2010 and Al-Odaini et al., 2013). Likewise, sulfonamides were detected in effluents from swine farms (Malintan & Mohd, 2006), and the residues were detected in chicken meat products (Cheong et al., 2010). Since sulfonamides have high potentials to resist degradation and are highly mobile (Luo et al., 2011), they could be extensively transported from pollution sources flowing surface water.

The Langat River basin is located in the southern part of the capital region (*i.e.* Klang Valley) in Peninsular Malaysia, and has a major role in regional water supply. Urbanization in the Langat River basin drastically progressed due to the acceleration of economic growth since the 1980s. As a consequence, surface runoff had increased with a positive relationship with urban-related land uses (Noorazuan et al., 2003). Moreover, water quality in the Langat River basin has deteriorated due to wastewater from industry and households, municipal waste and agricultural runoff (Juahir et al., 2011). Drinking water treatment facilities have been frequently shut down due to a high concentration of ammonia in intake water over the last two decades (Hasan et al., 2010).

According to our preliminary survey, surface water was heavily contaminated by *Escherichia coli* (*E. coli*) around urban sites and *E. coli* were detected even in upstream regions. It is probably because household coverage by piped sewers is inadequate and septic tanks are poorly maintained. Furthermore, there is no specific regulation or federal law for the livestock effluent standards except for the regulations that were enforced through various state enactments and by-laws. Therefore, farmers usually treat their wastewater by sedimentation ponds or any biological waste treatment systems. In addition, some livestock species such as cattle, dairy cow and goat were sometimes released to graze outside. Both insufficiently treated livestock effluents and the excrement left in grazing fields could be transported into rivers. Thus, these various point sources and non-point sources would result in the severe contamination of *E. coli*.

Likewise, severe environmental pollution of beta-agonists and sulfonamides is concerned in the Langat River basin. There are populated cities and towns located in mid catchment areas and a large scale of oil palm plantation and livestock farms around the southern part of the mid catchment areas and entire downstream areas. The variety of anthropogenic influence could cause the contamination of these drugs and make the pollution complicated to identify the sources by environmental monitoring. Therefore, a spatial analysis and a source profiling are also necessary to visualize the occurrence and distribution as well as to identify the pollution sources.

Distribution of contaminants in river basin is basically followed by elevation and flow direction of surface water in a gravitational way, which means that occurrence of contaminants detected in a sampling point is subject to its catchment area. The pollutant load could become proportional to a number of pollution sources (*i.e.* point source) and/or an area of pollution sources (*i.e.* non-point source) in the catchment area. As long as there is no significant regional difference of coverage of sewage treatment system and hydrological impacts like abstraction of river water among catchment areas, the pollutant load in surface water would have a correlation with the number and/or the area of pollution sources. If that is the case, the pollutant loads of beta-agonists and sulfonamides could have a correlation with human and/or livestock population, considering their usage for treatments. Therefore, this study aimed to analyze these drugs throughout the Langat River basin for clarifying the contamination, and also to conduct the spatial analysis and source profiling for identifying the pollution source by using geographic information system (GIS).

2. Material and methods

2.1. Standards and reagents

Fourteen beta-agonist standards (cimaterol, terbutaline, salbutamol, zilpaterol, cimabuterol, ractopamine, clenbuterol, brombuterol, tulobuterol, mabuterol, hydroxymethyl clenbuterol, clenpenterol, isoxsuprine and mapenterol), 2 beta-agonist surrogates (ractopamine-d3 and clenbuterol-d9) and 12 sulfonamide standards (sulfadiazine, sulfathiazole, sulfapyridine, sulfamerazine, sulfamethazine, sulfamethizole, sulfamethoxypyridazine, sulfadimethoxine, sulfaquinoxaline, sulfamethoxazole, sulfisoxazole and sulfachloropyridazine) were provided by Department of Veterinary Services in Ministry of Agriculture & Agro-Based Industry Malaysia. Methanol and acetonitrile were purchased from Fisher Scientific (USA).

2.2. Sampling sites and surface water collection

The locations of 14 sampling sites in the Langat River basin are shown in Fig. 1 and Table 1. The selection of the sampling sites was based on the main stream (*i.e.* the Langat River) and major tributaries. The sampling was conducted on the 22nd November, 2014. In each sampling site, surface water was collected by a stainless steel container and its one liter was filled into a polypropylene bottle. Meanwhile, pH and electrical conductivity (EC) were measured by LAQUAtwin (Horiba, Japan), and dissolved oxygen and water temperature were measured by Accumet AP84 (Fisher Scientific, Malaysia) on-site. Likewise, river width, water level and velocity in each sampling point were measured with a laser distance meter, a stopwatch, a water-level gauge and a plastic ball for estimating flow rate. The collected samples were put into a cooler box and transferred back to laboratory, and stored at 4 °C so as to prevent degradation of target compounds. The water samples were pretreated and analyzed by liquid chromatography–tandem mass spectrometry (LC–MS/MS) within 1 week after the sampling date.

2.3. Laboratory analysis

Chemical oxygen demand (CODMn), biochemical oxygen demand (BOD) and suspended solids (SS) were analyzed by standard methods. Ammonia nitrogen (NH_3-N) and phosphate-phosphorus (PO_4-P) were analyzed by a digital pack test apparatus (Digital Pack Test Multi, Kyoritsu Chemical-Check Lab. Corp., Japan). The number of *E. coli* was analyzed by Colilert method (IDEXX Laboratories Inc., USA).

2.4. Sample pretreatment

Sample pretreatments were separately taken for beta-agonists and sulfonamides in each water sample to fulfill acceptable recovery. In case of beta-agonists, 100 to 200 mL of the water samples were spiked with 10 μL of a surrogate standard, ractopamine-d3 (1 mg/L), and