

学校编码: 10384

密级\_\_\_\_\_

学 号: 33120121151639

厦 门 大 学

硕 士 学 位 论 文

九龙江流域表层水中农用有机化学品的  
污染特征和初步风险评价

Pollution Characteristics and Preliminary Risk Assessment of  
Organic Agrochemicals in Surface Water of Jiulong River Watershed

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论文提交日期: 2015 年 8 月

论文答辩时间: 2015 年 8 月

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## 摘要

农用化学品作为重要的农业生产资料之一,在提高农产品生产率方面发挥着重要作用。农药、兽药等农用有机化学品使用后可能通过干湿沉降、地表径流冲刷等途径进入水环境,威胁水生生态系统健康,导致饮用水源污染、食品安全等问题。

本论文选择常用的 40 类 210 种农药(包括氨基甲酸酯类、拟除虫菊酯类、酰胺类、唑类等)和 21 类 100 种兽药(包括大环内酯类、四环素类、磺胺类、性激素类等)作目标物,分别建立其在表层水中的分析方法,应用于九龙江流域北溪、西溪、河口农用有机化学品复合污染状况研究,并对水质安全和水环境生态风险进行了初步评价。主要研究内容及结果如下:

### 1. 表层水中多种类农药、兽药分析方法的建立

运用 LLE-GC-MS/MS 技术,建立了多种类农药的同时分析方法,210 种目标农药中有 197 种的方法检测限在 0.01-10.0 ng/L 之间;在 10 ng/L 和 50 ng/L 加标浓度下,河水基底中分别有 85.2%和 83.3%种目标物的回收率符合要求,相对标准偏差( $n=4$ )分别为 0.8%-25.3%和 0.1%-27.5%,海水基底中分别有 90.9%和 91.9%种目标物符合要求,相对标准偏差( $n=4$ )分别为 0.0%-25.4%和 1.3%-25.7%。

运用 SPE-HPLC-MS/MS 技术,建立了多种类兽药的分组同时分析方法,100 种目标兽药中有 84 种的方法检测限在 0.01-5.0 ng/L 之间;在 20 ng/L 和 100 ng/L 加标浓度下,河水基底中分别有 86%和 100%种目标物的回收率符合要求,相对标准偏差( $n=4$ )分别为 0.0%-17.6%和 0.1%-28.7%,海水基底中分别有 87%和 94%种目标物符合要求,相对标准偏差( $n=4$ )分别为 0.1%-8.8%和 0.1%-15.6%。

### 2. 九龙江流域表层水中农用有机化学品的 2014 年度污染特征研究

运用所建立的分析方法,于 2014 年 2、4、6、8、10、12 月对九龙江主要支流北溪、西溪及河口区共计 25 个站位采集,进行表层水中农药、兽药污染状况监测。结果表明:北溪、西溪、河口的农用有机化学品的站位检出总量分布在 105.2-1681.8 ng/L、137.4-1230.2 ng/L、44.4-856.5 ng/L 之间,大部分站位的枯水期检出总量较高;总计检出农药 83 种,站位检出总量在 16.0-1476.0 ng/L,不同站位在各水期表现不同;检出兽药 47 种,站位检出总量在 6.4-1034.6 ng/L,大部分站位表现为枯水期检出量>平水期>丰水期;检出频率较高的农药为氨基甲

酸酯类、苯胺类、酰胺类等，检出频率较高的兽药为磺胺类、氟甲砜霉素、林可霉素等。

3. 九龙江北溪、西溪表层水的水质安全评价和农用有机化学品水生生态风险初步评价。

本研究检出的农药、兽药较其他地区复杂；根据中国、美国、欧盟等的饮用水源水质标准，对北溪、西溪进行水质安全状况评价；采用商值法进行生态风险评价。北溪在 6-10 月水质安全状况较差，西溪在 4、10、12 月水质安全状况较差，分别有单项农药及检出总量超标，需要密切注意。北溪在各月份检出的农药中有 8%-15% 的项目处于高风险，兽药以四环素、林可霉素为高风险；西溪在各月份检出的农药中有 20% 的项目在中风险区以上，兽药以林可霉素为主要风险。总体上大部分农药、兽药的生态风险处于低风险区，高风险区以酰胺类农药、磺胺类抗生素和林可霉素为主要贡献。

**关键词：**农用有机化学品；农药；兽药；九龙江流域；表层水；污染特征；饮用水源；水质安全；生态风险评价

## Abstract

As essential production materials, agrochemicals are playing an important role in promoting agricultural production. Organic agrochemicals (OAC) including pesticides and veterinary drugs, enter aquatic environment through dry/wet precipitation, surface runoff etc. during pre- and post-use process, resulting in drinking water resources pollution and risk to aquatic ecosystem health..

In this study, multi-categorized pesticides and veterinary drugs were chosen as target compounds. Simultaneous analytical methods for target compounds in surface water were established and applied to pollution survey of OAC in the North Stream, West Stream, and estuary of Jiulong River, Fujian, China. Based on annual monitoring results, combined pollution characteristics of pesticides and veterinary drugs were summarized and identified. Water resource quality safety evaluation and preliminary aquatic ecological risk assessment were carried out. Research contents and results are as the following.

1. Establishment of simultaneous analytical methods for multi-categorized pesticides and veterinary drugs in surface water

Sensitive and accurate determination methods were established using LLE-GC-MS/MS for 210 pesticides and SPE-HPLC-MS/MS for 100 veterinary drugs in surface waters.

For 210 target pesticides, detection limits of 197 species were between 0.01 and 10.0 ng/L. At 10 ng/L and 50 ng/L spiking levels, Recoveries of 179 (85.2%) and 175 (83.3%) species in river water matrix met the criteria with relative standard deviations (RSD,  $n=4$ ) of 0.8%-25.3% and 0.1%-27.5%, and 191 (90.9%) and 193 (91.9%) species in sea water matrix met the criteria with RSD ( $n=4$ ) 0.0%-25.4% and 1.3%-25.7%, respectively.

For 100 target veterinary drugs, detection limits of 84 species were between 0.01 and 5.0 ng/L. At 20 ng/L and 100 ng/L spiking levels, 86 (86.0%) and 100 (100.0%) species in river water matrix met the criteria with RSD( $n=4$ ) of 0.0%-17.6% and 0.1%-28.7%, and 87 (87.0%) and 94 (94.0%) species in sea water matrix met the criteria with

RSD ( $n=4$ ) 0.1%-8.8% and 0.1%-15.6%, respectively

## 2. Pollution characterizes of organic agrochemicals in surface water of Jiulong River Watershed in 2014

The established methods were applied to the monitoring of pesticides and veterinary drugs pollution status in surface water samples collected in 25 stations from North Stream, West Stream and estuary of Jiulong River every 2 months ( February, April, June, August, October and December ) in 2014.

Results showed that the total OAC concentration detected in three areas (North Stream, West Stream and the estuary) were between 105.2-1681.8 ng/L, 137.4-1230.2 ng/L, 44.4-856.5 ng/L, which are much higher in dry season. Totally 83 pesticides were detected with concentration from 16.0 to 1476.0 ng/L. No certain tendency were observed among normal, rainy, and dry seasons. For target veterinary drugs, 47 species were detected with concentration ranging from 6.4 to 1034.6 ng/L. In most stations, the total concentration of detected veterinary drugs showed the tendency of dry season > normal season > rainy season. The most frequently detected pesticides were organochlorines, carbamates, azoles, amids and dinitroanilines, while the most frequently detected veterinary drugs were sulfonamides, lincomycin and florfenicol.

## 3. Water resource safety evaluation and preliminary ecological risk assessment of organic agrochemicals in surface water from North Stream, West Stream

The OACs detected in this study were much more complex compared with other region. The water resource quality and preliminary aquatic ecological risk in Jiulong watershed were assessed according to related water quality standards of China, USA and EU.

It is noticeable that the water quality in the North Stream during Jun to October is in relatively low quality status, while in West Stream was April, October and December, with individual and total OAC concentration exceeding criteria values. In North Stream, 8%-15% detected pesticides were evaluated as high risk class in every monitoring period, Tetracyclines and lincomycin were the major risk contributors. In West Stream, 20% of the detected OAC were higher than medium risk, lincomycin was the major risk contributor. In total, the ecological risks from most of the OACs are in low risk, except

for amids, lincomycin and sulfonamides.

Keywords: Organic agrochemicals (OAC); Pesticides; Veterinary drugs; Jiulong River Watershed; Surface water; Pollution characteristics; Drinking water resource; Water quality safety; Aquatic ecological risk assessment

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