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# 基于物种敏感度分布及相平衡理论的汾河流域磺胺类抗生素生态风险阈值研究

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**摘要:** 磺胺类抗生素(SAs)广泛应用于医疗、畜禽养殖等领域。但过量的 SAs 通过多种方式最终进入流域水体和沉积物中, 对流域生态系统带来潜在的风险。预测无效应浓度(PNEC)可以作为评估污染物潜在生态风险的阈值, 因此确定水体和沉积物中 SAs 的 PNEC 是风险评估的关键。本研究以黄河支流——汾河流域为研究区, 通过采集水体和沉积物的样品, 发现水体中 SAs 的磺胺甲恶唑(SMX)含量最高, 均值为  $73.6 \text{ ng} \cdot \text{L}^{-1}$ , 而磺胺醋酰(SAAM)检出率最高, 高达 100%。沉积物中仅检出了 2 种 SAs 类抗生素, 为磺胺醋酰(SAAM)和磺胺喹恶啉(SQX), 但检出频率却高达 100%。基于物种敏感度分布(SSD)得到水体中 SAs 的生态风险阈值为  $3.40 \sim 440 \text{ } \mu\text{g} \cdot \text{L}^{-1}$ 。在此基础上, 基于水-沉积物密度、体积比等参数, 采用相平衡理论(EqP)进一步得到了沉积物中 SAs 的生态风险阈值为  $0.065 \sim 75.5 \text{ mg} \cdot \text{kg}^{-1}$ 。基于确定的生态风险阈值, 对汾河流域 SAs 现状进行风险评估, 结果表明仅水体中的甲氧苄啶(TMP)的风险商(RQ)均值为 0.014, 存在一定的低风险, 但超标概率仅为 8%, 而其他类别在水体和沉积物中 RQ 均低于 0.01, 均无显著风险。

**关键词:** 磺胺类抗生素(SAs); 预测无效应浓度(PNEC); 物种敏感度分布(SSD); 相平衡理论(EqP); 生态风险阈值

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## Study on Ecological Risk Threshold of Sulfonamides Antibiotics in Fenhe River Basin Based on Species Sensitivity Analysis and Phase Equilibrium Theory

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**Abstract:** Sulfonamide antibiotics (SAs) are widely used in medical treatment, livestock and poultry breeding, aquaculture and other fields. However, excessive use of SAs enters the water and sediment of watershed through domestic sewage, surface runoff, and so on, resulting in potential risks for the ecosystem. Predicted no effect concentration (PNEC) can be regarded as the threshold for assessing the potential ecological risk of pollutants, therefore calculating the PNEC of SAs in water and sediment is the key to assess the ecological risk. In this study, through collecting samples of water and sediment in Fenhe River Basin, a tributary of the Yellow River, the results showed that the concentrations of sulfamethoxazole (SMX) in water were the highest, with an average of  $73.6 \text{ ng} \cdot \text{L}^{-1}$ , and the detection rate of sulfacetamide (SAAM) was the highest, with 100% detection rate. However, only two types of SAs, SAAM and sulfaquinoxaline (SQX), were detected in the sediments, with detection frequency as high as 100%. Based on species sensitivity analysis (SSD), the ecological risk threshold for SAs in water was obtained, ranging from 3.40 to  $440 \text{ } \mu\text{g} \cdot \text{L}^{-1}$ . Then, combined the density, volume ratio and other parameters of water and sediment, the ecological risk threshold of SAs in the sediment was also obtained using the method phase equilibrium theory (EqP), and the results were  $0.065 \sim 75.5 \text{ mg} \cdot \text{kg}^{-1}$ . Based on the ecological risk threshold of SAs in water and sediment in the Fenhe River Basin, the ecological risk was further assessed. The results showed that the average risk quotient (RQ) of trimethoprim (TMP) in water was 0.014, which could result in low risk with the probability of exceeding the threshold being only 8%. The RQ values of the other were all less than 0.01, indicating insignificant risk.

**Keywords:** sulfonamide antibiotics (SAs); predicted no effect concentration (PNEC); species sensitivity analysis (SSD); phase equilibrium theory (EqP); ecological risk threshold

磺胺类抗生素(sulfonamides, SAs)可通过抑制细菌细胞壁的合成等作用达到较好的临床治疗效果,并可促进机体生长,因此,被广泛应用于医疗、畜禽养殖以及水产养殖等领域<sup>[1-2]</sup>。但在提高人们生活质量的同时,抗生素出现过量使用现象。据统计,抗生素在进入体内后约有 30% ~ 90% 未经代谢而通过粪便和尿液排出<sup>[3]</sup>。过量的抗生素会导致抗生素母体及其代谢产物通过生活污水、生产废水等途径最终汇入流域水体中<sup>[4-5]</sup>。SAs 可以残留于流域水体中并长期在沉积物中积累,因此流域成为 SAs 的最终归宿<sup>[6-8]</sup>。流域中的 SAs 能够对水中微生物群落及水生生物造成危害,提高病菌的耐药性,并最终对生态、人体健康带来较高的风险<sup>[9-10]</sup>。

生态风险评估是量化有毒污染物生态危害程度的重要手段<sup>[11]</sup>。地表水的预测无效应浓度(predicted no effect concentration, PNEC)是欧盟风险技术指导文件针对现有的化合物风险评价提出的生态风险阈值,是化合物生态风险评价和管理的重要依据<sup>[12]</sup>。PNEC 值的大小对风险评估至关重要,因此确定合理的 PNEC 是风险评估的前提<sup>[13-15]</sup>。目前有多种方法来推导地表水的 PNEC 值,如评估因子<sup>[16]</sup>和物种敏感度分布(SSD)<sup>[17]</sup>。评估因子较为常见,此方法是通过最敏感物种的毒性数据计算得出风险阈

值<sup>[18-19]</sup>。近年来越来越多的研究人员开始使用 SSD 方法计算生态风险阈值<sup>[14,20]</sup>。SSD 是利用化学物对不同物种的毒性值构建物种敏感度分布曲线,计算一定程度受影响物种比例对应的污染物浓度<sup>[17,21]</sup>。

相比地表水研究,有关沉积物生态风险阈值的研究则相对滞后<sup>[22-24]</sup>。近年来研究者们采用相平衡理论(EqP)计算沉积物中污染物的风险阈值,目前已成为较受欢迎的方法之一<sup>[25-26]</sup>。EqP 通过污染物在水-沉积物之间的分配来计算风险阈值,因此水-沉积物的分配系数( $K_p$ )极为关键<sup>[20,27]</sup>。在大多数研究中, $K_p$  是通过水-正辛醇系数( $K_{ow}$ )和有机碳含量来确定<sup>[22-24]</sup>。然而  $K_p$  容易受到流域水环境中沉积物的颗粒组成、水沉积物体积比以及污染物含量等众多因素的影响<sup>[28-31]</sup>。因此,通过实测数据计算  $K_p$  以便获取沉积物中化合物的风险阈值成为当前的研究热点。

本研究选取黄河流域第二大支流——汾河流域为研究区,通过采集水体和沉积物样品,检测样品中 SAs 含量并分析其空间分布特征;基于本地水生生物的构成查找毒性数据库,并以此构建 SSD 曲线确定水体中 SAs 的风险阈值;在此基础上,结合水-沉积物体积比等因素进一步确定沉积物中 SAs 的风险阈值;最终,基于确定的风险阈值进行生态风险评估。

## 1 材料与方法 (Materials and methods)

### 1.1 样品采集及测定

汾河是黄河的一级支流,地处黄土高原生态脆弱区,发源于山西北部宁武县,经由6个地级市的34个县级市,最后由河津汇入黄河,全长716 km,流域面积39 741 km<sup>2</sup>(图1)。汾河流域面积约占山西省总面积的1/4,沿岸地区每年从汾河提取的水量占全省水资源利用总量的46%。作为山西省最大河流的汾河,支撑着超过全省1/3的人口,贡献着占全省近1/2的国民生产总值。与此同时,汾河也接纳了大量的污水,纳污量占到全省废污水总量的40%,对汾河的生态环境带来较大的威胁<sup>[32-33]</sup>。

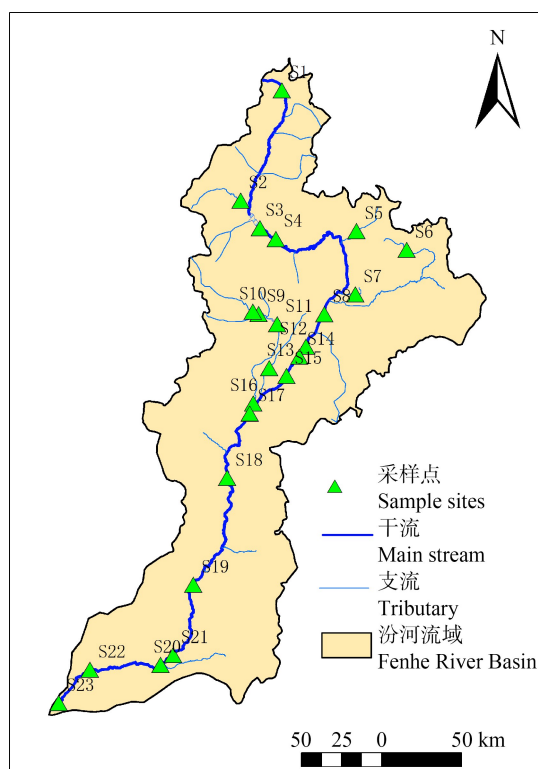


图1 汾河流域样品采集布点图

Fig. 1 Distribution of sample sites in Fenhe River Basin

本研究于2019年8月选取汾河流域源头、流经的主要城市、水库、畜禽养殖密集区、入黄河汇口以及主要支流等23个采样点,采集水体和沉积物样品进行检测分析(图1)。使用有机玻璃取水器采集水体样品,用1 L棕色玻璃瓶储存,采集时加入0.5 g的Na<sub>2</sub>-EDTA并用0.1 mol·L<sup>-1</sup>硫酸调节pH至4.0,并加入甲醇10 mL。使用彼得逊采泥器采集0~20 cm的沉积物样品,取大约1 kg装入1 L棕色玻璃瓶,加入0.5 g的Na<sub>2</sub>-EDTA。所有样品置于4℃采

样箱中,并于当天运回实验室待分析。分析的目标物包含10种磺胺类(SAs)抗生素:磺胺醋酰(SAAM)、磺胺嘧啶(SDZ)、磺胺噻唑(STZ)、磺胺吡啶(SPD)、磺胺甲基嘧啶(SMR)、磺胺异恶唑(SX)、磺胺二甲氧嘧啶(SDM)、磺胺喹恶啉(SQX)、甲氧苄啶(TMP)、磺胺甲恶唑(SMX)。详细检测方法和质量控制见有关文献<sup>[34]</sup>。

### 1.2 水体中生态风险阈值计算

预测无效应浓度(predicted no effect concentration, PNEC)是欧盟风险技术指导文件针对现有的化合物风险评价提出的生态风险阈值<sup>[35]</sup>。水体中SAs的PNEC使用如下公式计算:

$$PNEC_w = \frac{HC_5}{AF} \quad (1)$$

式中:HC<sub>5</sub>表示5%的生物体受到影响的危险浓度(μg·L<sup>-1</sup>),可通过物种敏感度分布(species sensitivity distribution, SSD)拟合得到<sup>[36]</sup>;AF是评估因子,通常取值为1~5。AF的选取具有不确定性,取值时需要考虑毒性数据信息量的丰富度、选取物种代表性和多样性、统计方法的不确定性和模型的拟合优度等。根据汾河流域特征,本研究AF取值为5<sup>[37]</sup>。

SSD是利用化学物对不同物种的毒性值构建物种敏感度分布曲线,计算一定程度受影响物种比例对应的污染物浓度<sup>[38-39]</sup>。SSD的基本假设是不同物种对特定污染物的敏感度能够用一些统计分布模型来描述,将多个物种的生态毒理学数据作为分布模型的样本,用于模型参数估计<sup>[40]</sup>。SSD采用分布模型包括Log-logistic分布函数、Burr III分布函数等来拟合毒性数据<sup>[41]</sup>,具体公式如下:

Log-logistic 分布函数:

$$F(x; \alpha, \beta) = \frac{1}{1 + \exp(-\frac{\lg(x) - \alpha}{\beta})} \quad (2)$$

Burr III 分布函数:

$$F(x; b, c, k) = \frac{1}{1 + (\frac{b}{x})^k} \quad (3)$$

式中:F(x)为毒性数据的累积分布函数;x为毒性数据(mg·L<sup>-1</sup>);α、β、b、c和k为模型参数。

本研究使用BurrIIZO计算软件构建SSD曲线。模型的准确性采用拟合优度评价。拟合优度的评价指标主要有均方根(RMSE)和残差平方和(SSE),两者越趋于0,表明拟合函数的拟合优度越好<sup>[42]</sup>。参考前期研究<sup>[34]</sup>,获取汾河流域水生生物组成,并基于

当地的物种组成查找对应的毒性数据。毒性数据主要来自美国环境保护局的 ECOTOX 数据库(<http://epa.gov/ecotox/>)、美国国家海洋和大气管理署(NOAA)的环境中药物数据库(<http://www.chbr.noaa.gov/peiar/>)以及瑞典 WiKiPharma 数据库([http://www.wikipharma.org/api\\_data.asp](http://www.wikipharma.org/api_data.asp))等。当同一个效应终点有多个可靠的毒性数据时,通过计算它们的平均值来保证一个物种只有一个毒性数据被使用<sup>[43]</sup>。

### 1.3 沉积物中生态风险阈值计算

沉积物中 SAs 的 PNEC 使用风险评估技术指导文件推荐的相平衡理论(EqP)计算<sup>[35]</sup>:

$$PNEC_s = \frac{K_{p,w-s}}{RHO_s} \times PNEC_w \times 1000 \quad (4)$$

其中:

$$RHO_s = F_{solid} \times RHO_{solid} + F_w \times RHO_w \quad (5)$$

$$K_{p,w-s} = \frac{c_s}{c_w} \quad (6)$$

式中: $PNEC_s$  为淡水沉积物环境预测无效应浓度(干质量计)( $\mu\text{g} \cdot \text{kg}^{-1}$ ); $PNEC_w$  为淡水环境预测无效应浓度( $\mu\text{g} \cdot \text{L}^{-1}$ ); $K_{p,w-s}$  为悬浮物-水分配系数( $\text{L} \cdot \text{kg}^{-1}$ ); $RHO_s$  悬浮物干体积密度; $RHO_w$  为水的密度,取  $1\,000\text{ kg} \cdot \text{m}^{-3}$ ;  $RHO_{solid}$  为实测的固相密度( $\text{kg} \cdot \text{m}^{-3}$ ); $F_{solid}$  为实测的沉积物中固体的体积分数; $F_w$  为实测的沉积物中水的体积分数; $c_s$  为实测的沉积相中抗生素浓度( $\mu\text{g} \cdot \text{kg}^{-1}$ ); $c_w$  为实测的水相中抗生素浓度( $\mu\text{g} \cdot \text{L}^{-1}$ )。

### 1.4 基于风险商值法的风险评估

采用风险商(RQ)对流域水体和沉积物中 SAs 的生态风险进行评估。RQ 分为 4 个风险水平:RQ < 0.01 为无显著风险;RQ 在 0.01 ~ 0.1 为低风险;RQ 为 0.1 ~ 1 为中等风险;RQ > 1 为高风险<sup>[44]</sup>。RQ 由以下方程计算<sup>[45]</sup>:

$$RQ = \frac{c}{PNEC} \quad (7)$$

式中: $c$  是抗生素的实测浓度(水体: $\mu\text{g} \cdot \text{L}^{-1}$ ,沉积物: $\mu\text{g} \cdot \text{kg}^{-1}$ );PNEC 是预测无效应浓度(水体: $\mu\text{g} \cdot \text{L}^{-1}$ ,沉积物: $\mu\text{g} \cdot \text{kg}^{-1}$ )。

## 2 结果(Results)

### 2.1 磺胺类抗生素空间分布特征及成因

水体中 SAs 类抗生素共检出 7 种,其中 SMX 含量最高,均值为  $73.6\text{ ng} \cdot \text{L}^{-1}$ ,而 STZ 的含量较低,均值仅为  $3.43\text{ ng} \cdot \text{L}^{-1}$ (图 2)。而 SMR、SX 和 SDM 均未检出。沉积物中 SAs 类抗生素仅检出 2 种,为 SAAM 和 SQX,均值分别为  $10.6\text{ }\mu\text{g} \cdot \text{kg}^{-1}$  和  $3.60\text{ }\mu\text{g} \cdot \text{kg}^{-1}$ ,但检出频率却高达 100%。空间上,水体中的 SAs 在中游整体较高,在上游及下游则较低(图 3)。而沉积物中的 SAs 在空间差异上则相对较小,变异系数仅为 0.26,但下游相对偏高。

### 2.2 水质和沉积物中磺胺类抗生素风险阈值分析

基于汾河流域水生生物组成,通过查询毒性库数据获取不同 SAs 类抗生素的毒性数据,建立 SSD

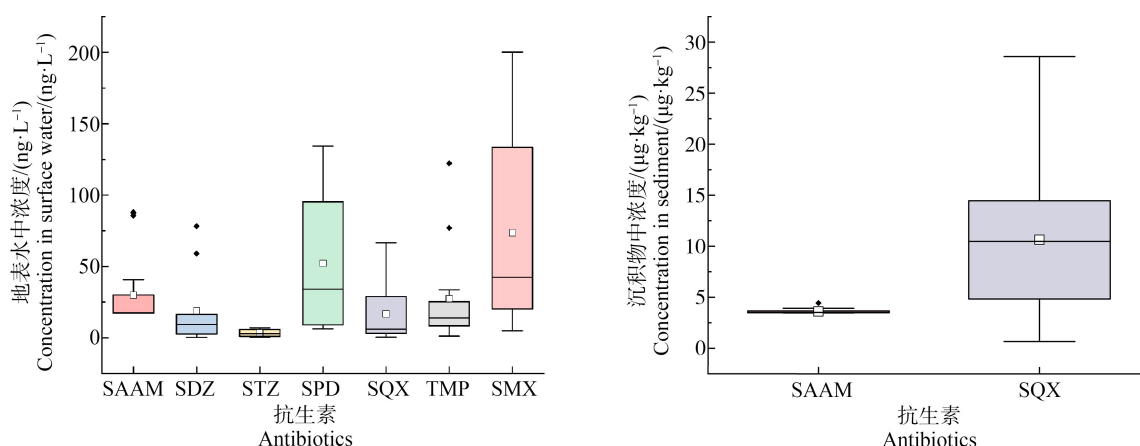


图2 汾河流域地表水及沉积物中磺胺类抗生素(SAs)含量箱体图

注:SAAM 表示磺胺醋酰,SDZ 表示磺胺嘧啶,STZ 表示磺胺噻唑,SPD 表示磺胺吡啶, SQX 表示磺胺喹恶啉,TMP 表示甲氧苄啶,SMX 表示磺胺甲恶唑。

Fig. 2 Concentration of sulfonamides (SAs) in water and sediments of Fenhe River Basin

Note: SAAM is the sulphacetamide, SDZ is the sulfadiazine, STZ is the sulfathiazole, SPD is the sulfapyridine, SQX is the sulfaquinolaxine, TMP is the trimethoprim, and SMX is the sulfamethoxazole.



曲线(表1)。由于 SMR、SQX、SAAM、SPD 查到的物种信息较少,不满足建立曲线的要求,因此仅对其他 6 种 SAs 类抗生素建立 SSD 拟合曲线(图 4)。SSD 曲线分布类型及参数见表 2。

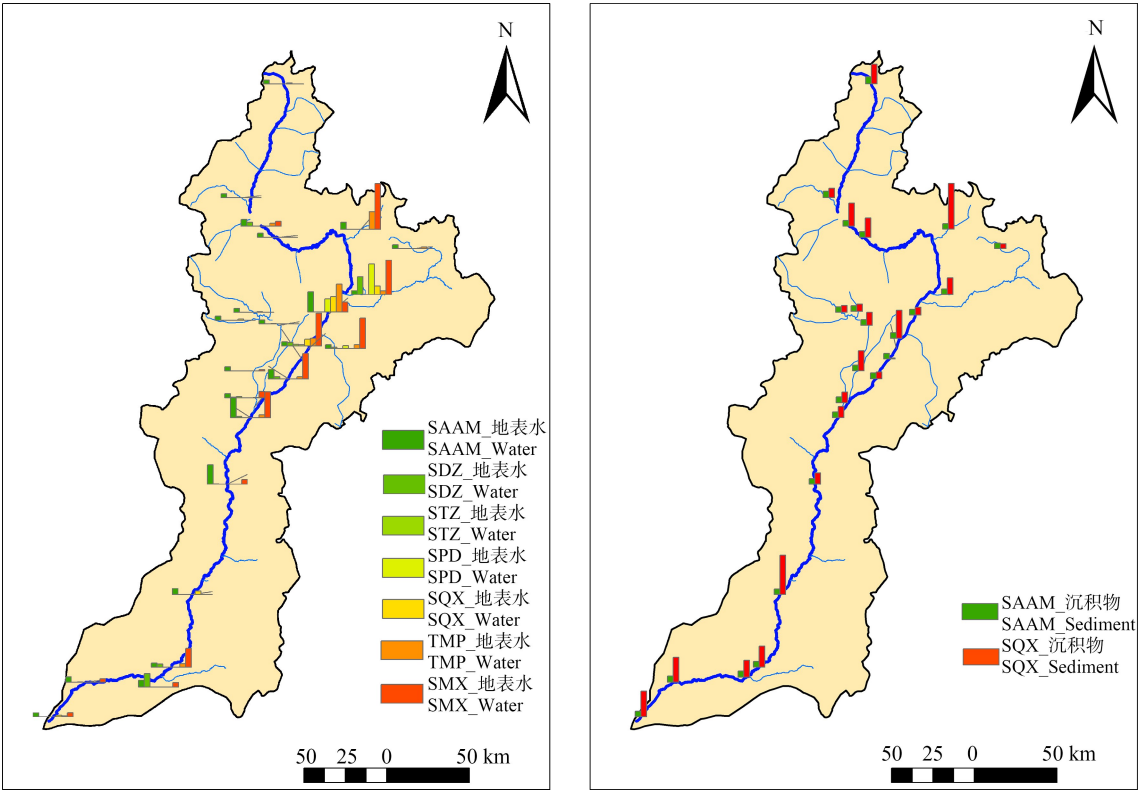


图 3 汾河流域地表水及沉积物中磺胺类抗生素空间分布

Fig. 3 Spatial variation of SAs in water and sediments in Fenhe River Basin

表 1 用于物种敏感度(SSD)曲线计算的毒性终点数据

Table 1 Endpoint concentration for species sensitivity distribution (SSD)

| 抗生素种类<br>Antibiotics  | 物种名称<br>The species                                | 毒性终点浓度均值/(mg·L <sup>-1</sup> )<br>Mean of toxicity endpoint/(mg·L <sup>-1</sup> ) |
|-----------------------|----------------------------------------------------|-----------------------------------------------------------------------------------|
| 磺胺嘧啶<br>Sulfadiazine  | 球等鞭金藻 <i>Isochrysis galbana</i>                    | 1.44                                                                              |
|                       | 淡色小球藻 <i>Chlorella fusca</i> var. <i>vacuolata</i> | 2.22                                                                              |
|                       | 亚头状假柯克氏藻 <i>Pseudokirchneriella subcapitata</i>    | 2.19                                                                              |
|                       | 铜绿微囊藻 <i>Microcystis aeruginosa</i>                | 0.135                                                                             |
|                       | 三角褐指藻 <i>Phaeodactylum tricornutum</i>             | 0.11                                                                              |
|                       | 大型溞 <i>Daphnia magna</i>                           | 112                                                                               |
|                       | 黑海胆 <i>Arbacia lixula</i>                          | 12.7                                                                              |
|                       | 宽紫海胆 <i>Paracentrotus lividus</i>                  | 59.76                                                                             |
|                       | 小球藻 <i>Chlorella vulgaris</i>                      | 1.34                                                                              |
|                       | 摇蚊幼虫 <i>Chironomus riparius</i>                    | 0.1                                                                               |
| 磺胺噻唑<br>Sulfathiazole | 淡色小球藻 <i>Chlorella fusca</i> var. <i>vacuolata</i> | 13.1                                                                              |
|                       | 小球藻 <i>Chlorella vulgaris</i>                      | 17.81                                                                             |
|                       | 大型溞 <i>Daphnia magna</i>                           | 193.4                                                                             |
|                       | 多刺裸腹溞 <i>Moina macrocopa</i>                       | 391.1                                                                             |
|                       | 青鳉 <i>Oryzias latipes</i>                          | 500                                                                               |

续表1

| 抗生素种类<br>Antibiotics     | 物种名称<br>The species                                | 毒性终点浓度均值/(mg·L <sup>-1</sup> )<br>Mean of toxicity endpoint/(mg·L <sup>-1</sup> ) |
|--------------------------|----------------------------------------------------|-----------------------------------------------------------------------------------|
| 磺胺异恶唑<br>Sulfisoxazole   | 花臂尾轮虫 <i>Brachionus calyciflorus</i>               | 9.63                                                                              |
|                          | 朝鲜臂尾轮虫 <i>Brachionus koreanus</i>                  | 0.1                                                                               |
|                          | 秀丽隐杆线虫 <i>Caenorhabditis elegans</i>               | 2.77                                                                              |
|                          | 鲫 <i>Carassius auratus</i>                         | 0.08                                                                              |
|                          | 网纹溞 <i>Ceriodaphnia dubia</i>                      | 15.51                                                                             |
|                          | 淡色小球藻 <i>Chlorella fusca</i> var. <i>vacuolata</i> | 1.54                                                                              |
|                          | 小球藻 <i>Chlorella vulgaris</i>                      | 1.57                                                                              |
|                          | 斑马鱼 <i>Danio rerio</i>                             | 109.16                                                                            |
|                          | 大型溞 <i>Daphnia magna</i>                           | 181                                                                               |
|                          | 水螅 <i>Hydra vulgaris</i>                           | 5                                                                                 |
| 磺胺二甲氧嘧啶 Sulfadimethoxine | 聚球蓝细菌 <i>Synechococcus</i> sp.                     | 760                                                                               |
|                          | 聚球藻 <i>Synechococcus leopoliensis</i>              | 1 100                                                                             |
|                          | 月芽藻 <i>Pseudokirchneriella subcapitata</i>         | 2.3                                                                               |
|                          | 海水派金虫 <i>Perkinsus marinus</i>                     | 10                                                                                |
|                          | 多刺裸腹溞 <i>Moina macrocopa</i>                       | 296.6                                                                             |
|                          | 惠氏微囊藻 <i>Microcystis wesenbergii</i>               | 470                                                                               |
|                          | 铜绿微囊藻 <i>Microcystis aeruginosa</i>                | 500                                                                               |
|                          | 斑点叉尾鲷 <i>Ictalurus punctatus</i>                   | 50                                                                                |
|                          | 大型溞 <i>Daphnia magna</i>                           | 204.5                                                                             |
|                          | 小球藻 <i>Chlorella vulgaris</i>                      | 11.2                                                                              |
|                          | 淡色小球藻 <i>Chlorella fusca</i> var. <i>vacuolata</i> | 9.85                                                                              |
|                          | 多变鱼腥藻 <i>Anabaena variabilis</i>                   | 1 500                                                                             |
|                          | 水华鱼腥藻 <i>Anabaena flosaquae</i>                    | 1 000                                                                             |
|                          | 柱胞鱼腥藻 <i>Anabaena cylindrica</i>                   | 480                                                                               |
| 甲氧苄啶 Trimethoprim        | 斑马贝 <i>Dreissena polymorpha</i>                    | 0.00029                                                                           |
|                          | 泽尼寡角摇蚊 <i>Diamesa zernyi</i>                       | 400                                                                               |
|                          | 大型溞 <i>Daphnia magna</i>                           | 100                                                                               |
|                          | 朝鲜臂尾轮虫 <i>Brachionus koreanus</i>                  | 0.01                                                                              |
|                          | 多变鱼腥藻 <i>Anabaena variabilis</i>                   | 11                                                                                |
|                          | 水华鱼腥藻 <i>Anabaena flosaquae</i>                    | 253                                                                               |
| 磺胺甲恶唑 Sulfamethoxazole   | 淡色小球藻 <i>Chlorella fusca</i> var. <i>vacuolata</i> | 1.54                                                                              |
|                          | 网纹溞 <i>Ceriodaphnia dubia</i>                      | 15.51                                                                             |
|                          | 大型溞 <i>Daphnia magna</i>                           | 181                                                                               |
|                          | 斑马鱼 <i>Danio rerio</i>                             | 109.16                                                                            |
|                          | 鲫 <i>Carassius auratus</i>                         | 0.08                                                                              |
|                          | 鼓凸浮萍 <i>Lemna gibba</i>                            | 0.13                                                                              |
|                          | 朝鲜臂尾轮虫 <i>Brachionus koreanus</i>                  | 0.1                                                                               |
|                          | 水螅 <i>Hydra vulgaris</i>                           | 5                                                                                 |
|                          | 秀丽隐杆线虫 <i>Caenorhabditis elegans</i>               | 2.77                                                                              |

注:表中抗生素浓度均是有效成分浓度。

Note: The concentrations of antibiotic in the table are all the active ingredient concentrations.

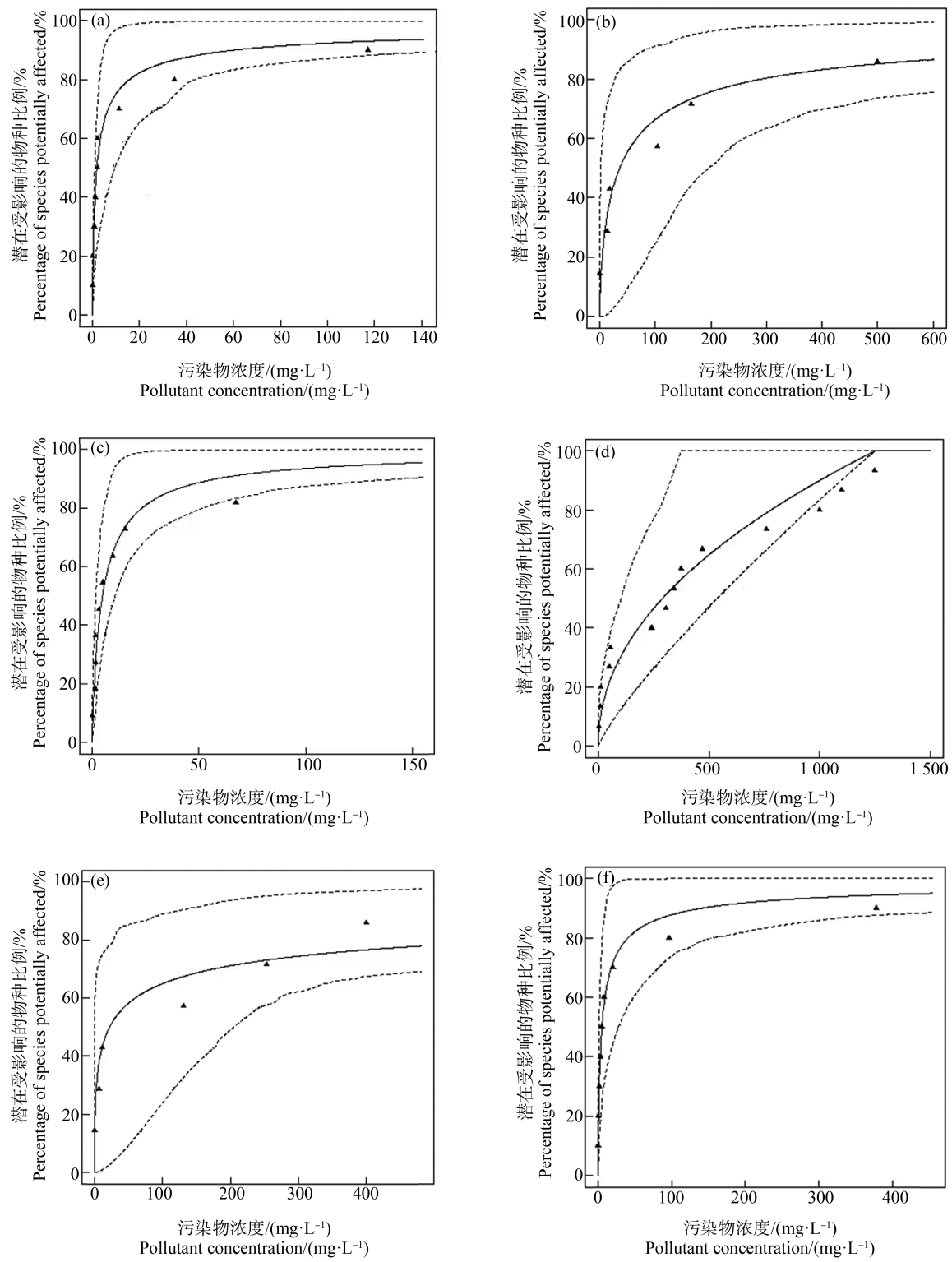


图 4 汾河流域磺胺类抗生素 SSD 曲线

注: (a) 磺胺嘧啶(SDZ); (b) 磺胺噻唑(STZ); (c) 磺胺异恶唑(SX); (d) 磺胺二甲氧嘧啶(SDM); (e) 甲氧苄啶(TMP); (f) 磺胺甲恶唑(SMX)。

Fig. 4 The SSD curve of SAs in Fenhe River Basin

Note: (a) Sulfadiazine (SDZ); (b) Sulfathiazole (STZ); (c) Sulfisoxazole (SX); (d) Sulfadimethoxine (SDM); (e) Trimethoprim (TMP); (f) Sulfamethoxazole (SMX).

表 2 汾河流域磺胺类抗生素分布曲线类型及参数  
Table 2 Type and parameters of SSD curve for SAs in Fenhe River Basin

| 抗生素名称<br>Antibiotics | 分布类型<br>Type of curves | $b(\alpha)$ | $\alpha(\beta)$ | $k$   |
|----------------------|------------------------|-------------|-----------------|-------|
| SDZ                  | Burr type III          | -1.47       | -0.55           | 0.97  |
| STZ                  | Log-logistic           | 3.58        | -0.41           |       |
| SX                   | Burr type III          | 1.60        | -0.12           | -0.01 |
| SDM                  | Log-logistic           | -0.75       | -7.13           |       |
| TMP                  | Log-logistic           | 3.09        | -0.89           |       |
| SMX                  | Burr type III          | 0.92        | -0.45           | 0.35  |

通过 SSD 拟合曲线获取  $HC_5$  值并计算水体中 SAs 类抗生素的  $PNEC_w$ (表 3)。在此基础上,基于抗生素实测数据计算  $K_p$ ,结合  $F_{soild}$  等参数<sup>[46]</sup>,进一步得到了沉积物中 SAs 类抗生素的  $PNEC_s$ (表 3)。结果表明,水体 SAs 类抗生素的风险阈值整体较高,均值达到了  $99.4 \mu g \cdot L^{-1}$ 。其中,TMP 的风险阈值最低,仅  $3.40 \mu g \cdot L^{-1}$ ,而 SDM 的风险阈值最高,高达  $440 \mu g \cdot L^{-1}$ 。沉积物风险阈值均值为  $15.7 mg \cdot kg^{-1}$ ,TMP 的风险阈值仍是最低,为  $0.065 mg \cdot kg^{-1}$ ,最高的是 STZ,为  $75.5 mg \cdot kg^{-1}$ 。水体中不同抗生素之间的差异性较高,标准偏差高达  $169.2 \mu g \cdot L^{-1}$ ,而沉积物中的抗生素的标准偏差仅为  $30.0 mg \cdot kg^{-1}$ 。TMP 作为磺胺类抗生素的增效剂,可通过降低耐药菌株产生的概率,经人体吸收后广泛地分布于全身的组织 and 体液中,可以在生物体内维持较长时间的抑菌效果,故而导致其毒性较高<sup>[47]</sup>。而 SDM 是通过干扰细菌对叶酸的代谢而抑制细菌的繁殖,其性质稳定,其毒性较低<sup>[48]</sup>。

表 3 基于 SSD 方法建立的汾河流域磺胺类抗生素风险阈值  
Table 3 Risk threshold of SAs in Fenhe River Basin based on SSD method

| 抗生素名称<br>Antibiotics | $HC_5$<br>$/(mg \cdot L^{-1})$ | $PNEC_w$<br>$/( \mu g \cdot L^{-1})$ | $PNEC_s$<br>$/(mg \cdot kg^{-1})$ |
|----------------------|--------------------------------|--------------------------------------|-----------------------------------|
| SDZ                  | 0.064                          | 12.8                                 | 0.301                             |
| STZ                  | 0.42                           | 84.0                                 | 75.5                              |
| SX                   | 0.17                           | 34.0                                 | 1.24                              |
| SDM                  | 2.2                            | 440                                  | 16.9                              |
| TMP                  | 0.017                          | 3.40                                 | 0.065                             |
| SMX                  | 0.11                           | 22.0                                 | 0.480                             |

2.3 汾河流域水体和沉积物磺胺类抗生素风险评估  
基于 SSD 法计算的 SAs 类抗生素的生态风险阈值,对汾河流域水体和沉积物中的 SAs 类抗生素

进行风险评估(图 5)。结果表明,沉积物中所有点位均未达到显著风险水平,水体中 TMP 的 RQ 值最高,为 0.014,其他均低于 0.01。说明除水体中的 TMP 外,汾河流域水体和沉积物中的 SAs 类抗生素均不会带来生态风险。但 TMP 超标概率仅为 8%。空间上,仅在点 S5 和 S8 存在一定的低风险,S5 的 RQ 为 0.013、S8 的 RQ 为 0.012。其中 S5 是杨兴河支流,S8 是汾河中游太原段下游。杨兴河支流流经阳曲县,阳曲县发达的养殖业可能对水体中 TMP 存在较大影响<sup>[49]</sup>。但由于其高水溶性的性质,反而沉积物中不存在风险。而 S8 不仅承接了汾河太原段的生产生活中 SAs 类抗生素的排入,还通过太榆退水渠汇集了晋中市的生活污水,这也可能造成了水体中 TMP 存在风险现状。

3 讨论 (Discussion)

在汾河流域中,支流和干流上游水体中 SAs 类抗生素含量均较低,这些区域一般地处山区,是重要的水源地,人类活动较少。抗生素的生产和使用与人为活动紧密相关,较少的人员活动使得这些区域抗生素残留较少<sup>[50]</sup>。汾河中游属于太原盆地和晋中盆地,是重要的工业区域,养殖业也较发达,导致 SAs 类抗生素在这些区域检出浓度较高<sup>[51-53]</sup>。而沉积物中 SAs 类抗生素在中游较低而下游较高,说明随着水体向下游流动,更多的 SAs 类抗生素被携带进入下游,并逐渐进入和累积于沉积物中<sup>[54-55]</sup>。

在本研究的 SSD 法计算过程中,包含了多个营养等级,且在部分物种存在多个毒性数据的情况下取其均值,以尽可能减小其不确定性<sup>[37,56]</sup>。此外,在以往的沉积物风险研究中,由于沉积物中的毒性数据有限,研究人员通常将沉积物浓度转换为孔隙水浓度,然后根据水质基准计算沉积物风险,这种方法未能反映水-沉积物的区域特征<sup>[22-23,45]</sup>。本研究基于



实地样品采集,计算土壤质地和泥沙中水分含量等参数,根据热力学平衡原理,计算出泥沙质量基准<sup>[20]</sup>,利用测量的沉积物基准来评估污染物的生态风险更为科学<sup>[27]</sup>。另外,以往研究者们多基于沉积物中的辛醇-水分配系数( $K_{ow}$ )和有机碳含量(%)将

沉积物中污染物浓度折算为孔隙水浓度,进而使用水体风险阈值评估其风险水平<sup>[57]</sup>。然而,分配系数在不同区域差别较大,故该方法存在一定的局限性<sup>[23]</sup>。此外,汾河流域作为黄河主要支流的,泥沙含量较高,泥沙对结果可能产生重要的影响<sup>[58]</sup>。

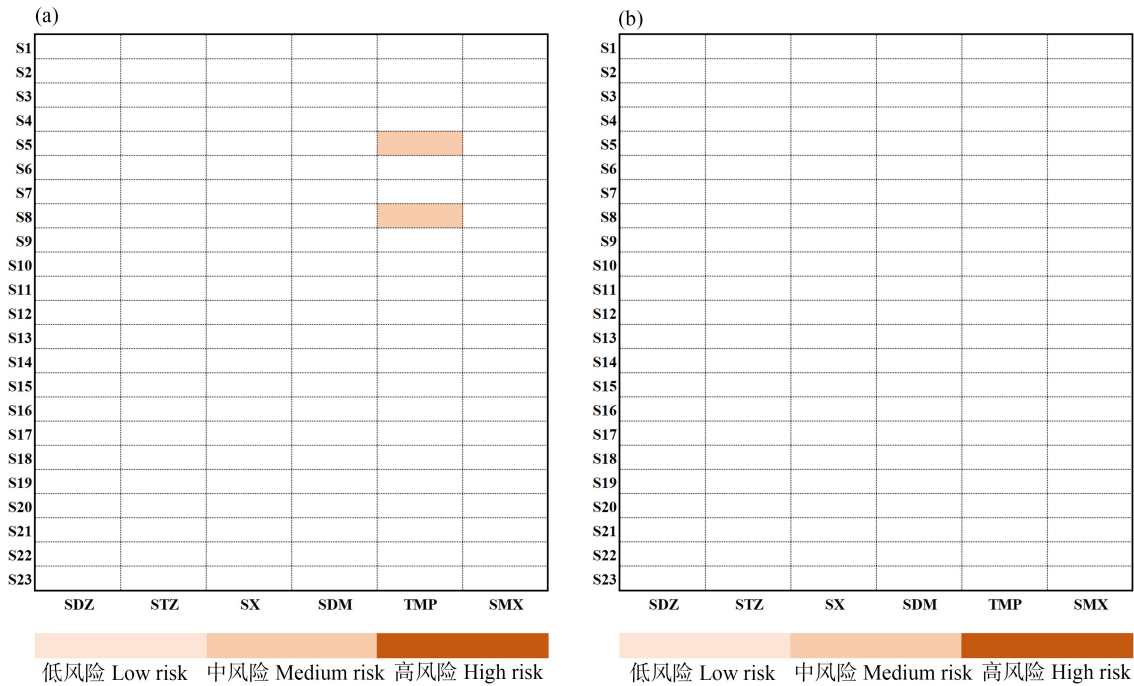


图 5 汾河流域磺胺类抗生素风险分布

注:(a) 地表水;(b) 沉积物

Fig. 5 Risk assessment of SAs in Fenhe River Basin

Note: (a) Water; (b) Sediment

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