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海水养殖用塑料中有机磷酸酯的溶出规律及生物富集特征*

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摘要　养殖用塑料的长期使用不可避免地造成塑料添加剂溶出到水环境中。然而，这些塑料添加剂的溶出规律及对水生生物的暴露风险尚不清晰。本研究聚焦典型塑料添加剂有机磷酸酯(OPEs)，以在野外海水养殖塘中收集的塑料防渗膜为研究对象，分别进行室内模拟溶出实验和水生生物暴露实验。结果显示，在 240 h 的模拟溶出实验中，总 OPEs 的溶出量为 12.24 ng/g。其中，含氯类 OPEs 的溶出率相对较高，磷酸三(2-氯乙基)酯(TCEP)溶出率达到了 40.6%，含氯类 OPEs、芳香类 OPEs、烷烃类 OPEs 溶出率依次降低；塑料防渗膜在 0~2 d 的溶出实验过程中，OPEs 的溶出速率最快，在第 6 天后，溶出速率开始达到平衡状态。水生生物暴露实验结果显示，48 h 内防渗膜溶出的 OPEs 在卤虫(*Artemia*)体内检出 5 种，其中，磷酸三甲苯基酯(TCP)、磷酸三(1,3-二氯异丙基)酯(TDCPP)的 $\log_{10}$BAF (生物富集因子)均大于 3.7，具有生物富集效应；磷酸三正丁酯(TnBP)的 $\log_{10}$BAF 值介于 3.3~3.7 之间，具有潜在的生物富集效应。上述结果表明，海水养殖塘中的塑料防渗膜所释放的 OPEs 会对水生生物造成潜在的风险。

关键词　养殖用塑料；有机磷酸酯；溶出规律；生物富集
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现代海水养殖业的迅速发展往往伴随着塑料制品的大量使用，包括绳索、浮球、网箱、塑料管、养殖池防渗膜及泡沫包装盒等塑料制品，用于搭建养殖设施及运输水产品(Vázquez-Rowe *et al*, 2021; 凌爱军等, 2024)。养殖用塑料制品在使用时，不可避免地发生老化、磨损和裂解(夏斌等, 2019)，且该过程将导致塑料添加剂向养殖水体中溶出。已有研究调查了养殖区和非养殖区河流、湖泊及海域中的塑料添加剂，发现塑料添加剂在养殖区的浓度高于非养殖区(曾维斌等, 2020; Zhang *et al*, 2020; Liu *et al*, 2022)。养殖用塑料制品是部分水域各类塑料添加剂污染的重要来源(Lin *et al*, 2023)。例如，研究发现，环境中溴代阻燃剂六溴环十二烷(hexabromocyclododecanes, HBCDs)可从聚苯乙烯浮标中大量且快速地溶出，导致养殖区水体中含有高浓度的 HBCDs，证实浮标是 HBCDs 的主要来源(Al-Odaini *et al*, 2015, Jang *et al*, 2016)。

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曾维斌(2019)在研究北部湾某海水养殖区有机磷酸酯(organophosphate esters, OPEs)污染特征时发现，养殖鱼塘使用的防渗膜、增氧机等塑料制品中添加的 OPEs 也会释放到水环境中。尽管这些研究发现了塑料添加剂的溶出，然而目前有关这些塑料添加剂的溶出规律的研究十分有限。

此外，在养殖过程中，水产品在生长期间可能会接触到渔业养殖用塑料制品释放的溶出物(Hou *et al*, 2016)。例如，有研究表明，欧洲养殖贻贝中的 OPEs 浓度较高(Aznar-Alemany *et al*, 2018)，荷兰养殖虾中的 HBCDs 浓度意外地高(van Leeuwen *et al*, 2009)，这是因为生物体在生长期间与含有 OPEs 和 HBCDs 的塑料工具密切接触。其他相关研究也得到相似的推论，例如，Chessa 等(2019)发现，与非养殖区相比，HBCDs 在养殖区鱼类和贝类中的含量明显更高，推测养殖区的塑料制品浮标为 HBCDs 潜在污染源。上述研究表明，养殖用塑料释放的各种溶出物可被生物组织吸收，导致其在养殖区水产品中的浓度高于野生水产品(Garcia-Garin *et al*, 2020)。

OPEs 作为一种典型的塑料添加剂，其在水生生物体内的富集问题已受到广泛关注(Hou *et al*, 2017; Wang *et al*, 2019; Zhang *et al*, 2018; van Den Eede *et al*, 2013; Giulivo *et al*, 2017; Teo *et al*, 2015)。然而，国内外关于 OPEs 的生物富集研究大多集中在野外调查，缺乏系统的室内研究。因此，本研究以 OPEs 作为研究对象，针对海水养殖塘这一相对封闭的生态系统中的塑料防渗膜，实地调查其中 OPEs 的种类及其赋存水平；并改变传统静态溶出的方式，通过动态溶出的方式模拟室外溶出情况，明确 OPEs 从防渗膜中溶出的规律；相对于传统的人为添加 OPEs 的暴露方式，本研究采用塑料防渗膜进行生物暴露实验，对探明其中溶出的 OPEs 在卤虫(*Artemia*)体内的富集特征具有实际意义，研究结果将为海水养殖用塑料中添加剂的使用和管理提供有益参考。

1　材料与方法

1.1　化学品与试剂

主要标准品：目标化合物标准品磷酸三乙酯(triethyl phosphate，TEP，99.5%)、磷酸三甲酯(trimethyl phosphate，TMP，99.7%)、磷酸三正丙酯(tri-*n*-propyl phosphate，TNPP，99.8%)、磷酸三异丙酯(triisopropyl phosphate，TiPP，95.3%)、磷酸三异丁酯(triisobutyl phosphate，TiBP，99.7%)、磷酸三戊酯(tri-*n*-amylphosphate，TPTP，99.9%)、磷酸三(2-丁氧基乙基)酯[tris (2-butoxyethyl) phosphate，TBOEP，97.6%]、磷酸三(1，3-二氯异丙基)酯[tris (1,3-dichloro-2-propyl) phosphate，TDCPP，94.6%]购置于中国坛墨质检公司，磷酸三正丁酯(tributyl phosphate，TnBP，99.0%)、磷酸三(2-氯乙基)酯[tris (2-chloroethyl) phosphate，TCEP，98.0%]、磷酸三苯酯(triphenyl phosphate，TPHP，99.9%)购于北京曼哈格公司，磷酸三(氯异丙基)酯[tris (1-chloro-2-propyl) phosphate，TCPP，99.5%]购于 Aladdin，磷酸三甲苯基酯[tris (methylphenyl) phosphite，TCP，98.17%]购于上海甄准生物公司，13 种 OPEs 的基本信息见表 1 和图 1。实验中所使用的试剂甲醇、乙腈、正己烷均为色谱纯(CNW，中国)、乙酸乙酯色谱纯(Macklin，中国)、甲酸色谱纯(科密欧，中国)。

表 1　13 种 OPEs 的理化性质

Tab.1　The physical and chemical properties of 13 OPEs

化合物 Compounds	分子量 Molecular weight	辛醇-水分配系数 $\log K_{ow}$	水溶解度 S_w/(g/L)
TEP	182.15	0.8	5.0×10^{2}
TnBP	266.31	4	0.3
TMP	140.07	–0.7	5.0×10^{2}
TnPP	224.23	1.9	6.5
TiPP	224.23	2.2	7.5
TiBP	266.31	3.5	1.6×10^{-2}
TPTP	308.39	5.2	1.6×10^{-4}
TBOEP	398.47	3.8	1.1
TCEP	285.49	1.4	7.0
TCPP	327.57	2.6	1.2
TDCPP	430.90	3.7	7.0×10^{-3}
TPHP	326.28	4.6	1.9×10^{-3}
TCP	368.36	5.1	3.6×10^{-2}

1.2　养殖用塑料的收集及 OPEs 的赋存

防渗膜的采集：用剪刀在旧养殖鱼塘底部剪取一块(图 2a、b)，用纯水冲洗，轻擦去膜表面的尘土。用剪刀将防渗膜剪成 5 mm × 5 mm 的小块，称取 0.5 g 加入 10 mL 玻璃离心管，加入 8 mL 乙酸乙酯：正己烷(V：V=3：2)，放入振荡培养箱中 12 h。振荡培养后取出，超声提取 30 min，取 1 mL 上清液，氮吹至近干，使用 1 mL 甲醇定容，用 2 mL 色谱瓶储存于–20 ℃冰箱，待 UPLC-MS/MS 分析。

1.3　OPEs 室内模拟动态溶出实验

将塑料防渗膜剪成 5 mm×5 mm 的小块，称取约

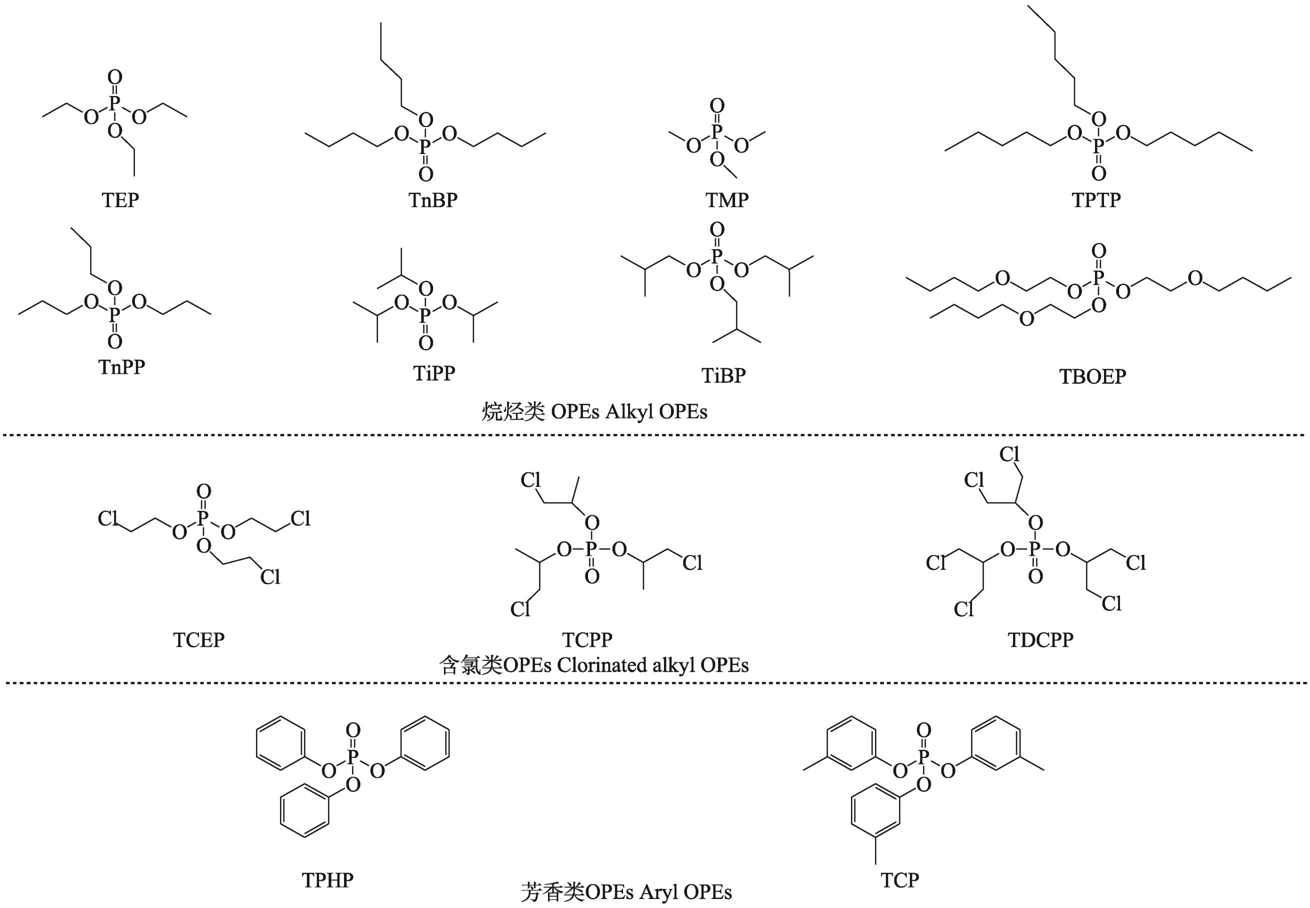

图 1 13 种 OPEs 结构式
Fig.1 Structural formulas of thirteen OPEs

5.0 g 置于光化学反应器(CEL-LB70，中教金源，中国)中的玻璃反应管中。设置空白组(不添加防渗膜)和实验组各 4 个平行。溶出使用的介质为人工海水(盐度 30)，温度为 25 ℃。光源采用长弧氙灯模拟太阳光照强度(输入功率 500 W)启动开始老化，使用光功率计测量为(96±20) mW/cm^2。采用蠕动泵模拟实际环境的流动条件，采用 HLB 固相萃取柱(6 mL，CNW，中国)收集防渗膜溶出的 OPEs。老化总时长为 240 h，每 48 h 更换一支固相萃取柱。采用 6 mL 超纯水和 6 mL 乙腈进行洗脱，氮气浓缩，1 mL 甲醇定容。保存至–20 ℃，待后续 UPLC-MS/MS 分析。

1.4 卤虫短期暴露实验

将 60 只成体卤虫放入 500 mL 人工海水中(盐度 35)。根据《DB11/T 1869-2021 池塘养殖通用技术规范》中海水养殖池塘规格计算防渗膜的面积尺寸为 2.1 cm×2.1 cm，并直接放入 500 mL 人工海水中。实验设置对照组(不添加防渗膜)和实验组，每组设 3 个平行组，每组平行进行 3 个重复。实验的环境条件：光照强度为 1 000 lx，温度为 25 ℃，光暗比(12∶12)。暴露时间为 48 h，期间不喂食。暴露时间结束后，取出卤虫，并保留水样。生物样本处理方法参照丁锦建等(2017)的研究方法，取 0.1 g 卤虫加入 2 mL 0.5%酸化乙腈，超声提取 15 min，加入 40 mg NaCl 和 160 mg $MgSO_4$，涡旋 1 min，3 000 r/min 离心 5 min。取上清液加入 20 mg PSA、20 mg C_{18} 和 120 mg $MgSO_4$ 进行净化，涡旋 30 s，5 000 r/min 离心 5 min，取上清液，氮吹近干，用甲醇定容至 1 mL 于色谱瓶中，保存于–20 ℃，待后续 UPLC-MS/MS 分析。卤虫及水样检测回收率见表 2。

1.5 仪器方法

使用高效液相色谱(AB Sciex ExionLCTM AD)串联三重四极杆串联质谱仪(AB Sciex Qtrap6500+)测定样品中 OPEs 的含量，色谱柱为 ACQUITY UPLC BEH C18 (2.1 mm×100 mm，1.7 μm)；采用 95%乙腈和 0.1%甲酸水溶液作为流动相进行梯度洗脱，时间共计 12 min，流速为 0.3 mL/min，进样量为 2 μL，柱温为 40 ℃。质谱采用正离子模式，具体质谱信息见表 3。

表 2　溶出水样及卤虫体内 OPEs 检测方法及评价

Tab.2　Detection methods and evaluation of OPEs in dissolved water samples and *Artemia* bodies

OPEs 种类 OPEs type	保留时间 Retention time /min	检出限 Limit of detection/(ng/L)		加标量 Spike quantity /(μg/L)	加标回收率 Recovery rate/%	
		水样 Water sample	卤虫 *Artemia*		水样 Water sample	卤虫 *Artemia*
TEP	3.10	0.08	0.22	50	89	40
TnBP	6.30	0.01	0.11	50	99	78
TMP	1.60	0.28	0.22	50	5	27
TnPP	4.85	0.05	0.10	50	84	68
TiPP	4.39	0.05	0.10	50	89	21
TiBP	6.04	0.01	0.11	50	94	78
TPTP	7.23	0.01	0.06	50	52	86
TBOEP	6.40	0.02	0.11	50	94	103
TCEP	3.94	0.17	0.25	50	98	70
TCPP	4.96	0.32	0.27	50	130	93
TDCPP	5.73	0.45	0.28	50	113	68
TPHP	6.03	0.27	0.16	50	105	72
TCP	6.97	0.05	0.27	50	95	74

表 3　13 种 OPEs 的质谱信息

Tab.3　Mass spectrometry information of thirteen OPEs

化合物 Compounds	保留时间 Retention time/min	母离子 Precursor ion	子离子 Production	碰撞能量 CE	去簇电压 DP
TEP	3.32	183.1	99.0/127.1	22/15	45/30
TnBP	6.46	267.2	155.2/211.0	14/12	39/37
TCEP	4.26	285.5	99.0/124.9	30/21	47/27
TPHP	6.39	327.3	98.9/175.0	47/35	129/115
TCPP	5.31	327.0	98.9/175.0	28/17	30/1100
TMP	1.66	141.0	109.0/78.9	22/30	51/33
TnPP	5.04	225.3	98.9/141.2	12/20	19/46
TiPP	4.74	225.1	98.9/183.1	20/10	35/30
TiBP	6.45	267.3	155.2/194.9	12/12	34/58
TPTP	7.65	309.3	98.9/169.0	23/15	40/19
TBOEP	6.76	399.2	199.3/299.3	21/16	68/85
TDCPP	6.09	431.1	98.9/209.1	29/22	51/58
TCP	7.37	369.3	166.0/243.2	38/37	130/135

1.6　数据处理

利用溶出率来表示 OPEs 的溶出水平，如公式(1)所示：

$$\varepsilon_{rc}=\frac{C_{rc}}{C_{fc}}\times\% \tag{1}$$

利用溶出速率表示 OPEs 某一时间段内溶出量的水平，如公式(2)所示：

$$v_{rc}=\frac{C_{rc}}{\Delta t} \tag{2}$$

式中，ε_{rc} 表示溶出率(%)；C_{rc} 表示防渗膜中 OPEs 溶出的浓度(ng/g)；C_{fc} 表示防渗膜中 OPEs 赋存的浓度(ng/g)；v_{rc} 表示溶出的速率(ng/h)；Δt 表示溶出的时间(h)。

存活率表示卤虫在暴露实验中的存活数量与实验总数量之比，如公式(3)所示：

$$存活率=\frac{存活数量}{实验总数量}\times 100\% \tag{3}$$

生物富集评价，采用生物富集因子(BAF)，当化

合物的 BAF>5 000 或($\log_{10}$ BAF>3.7)时，该化合物定义为具有潜在生物富集效应的物质(EU, 2006)。如公式(4)表示：

$$BAF = \frac{C_{biota}}{C_{water}} \quad (4)$$

式中，C_{biota} 表示生物体内的 OPEs 浓度(ng/kg)；C_{water} 表示水中的 OPEs 浓度(ng/L)。

1.7 统计学方法

采用单因素方差分析(one-way ANOVA)检验防渗膜溶出 OPEs 种类及不同组别卤虫体内 OPEs 含量之间的差异性(SPSS 22.0 软件)，对存在差异的组别进行多重比较检验，差异显著性水平为 $P<0.05$。对于防渗膜的溶出速率中不同 OPEs 和不同时间段对于溶出速率的影响，采用多因素方差分析检验。

2 结果与讨论

2.1 塑料防渗膜中 OPEs 的赋存

如图 2a 所示，塑料防渗膜采集自养殖塘，位于海口市群尚村(20.03°N，110.44°E)。测得 OPEs 的含量为 625.99 ng/g，其种类共 6 种，包括烷烃类 OPEs (TnBP 和 TiBP)，芳香类 OPEs (TCP)和氯代类 OPEs (TCEP、TDCPP 和 TCPP)。其中，TCPP 在防渗膜中的含量最高，达到(395.15±48.05) ng/g，占总量的 63.12%，其余为 TnBP [(52.96±5.25) ng/g]。TCP 赋存占比最低，仅有 0.33%。TCPP 作为一种氯代类阻燃剂，在环境中较为稳定，不易降解(Liu *et al*, 2019; Chen *et al*, 2021; Cristale *et al*, 2016)。而与之相反，TCP 的含量较少，这可能是因为其作为芳香类的 OPEs，在环境中不稳定，在自然老化的塑料防渗膜中易挥发和降解，以有机磷酸二酯的形式存在于水环境中(Su *et al*, 2016)。本研究中 OPEs 在防渗膜中的赋存含量与其他塑料中 OPEs 的赋存含量水平相当，如塑胶跑道中总 OPEs 的赋存含量为 52.37~534.89 ng/g (印红玲等, 2017)；塑料食品包装袋中总 OPEs 的平均含量为(307±606) ng/g (Bi *et al*, 2023)；塑料食品包装中$\sum_3$OPAs 和$\sum_3$OPEs 分别为<方法定量限(method quantification limit，MQL)~24 ng/g、196~831 ng/g (Xing *et al*, 2023)。然而，塑料防渗膜所处的养殖塘属于封闭环境，且在海水中的长期暴露，不可避免地造成 OPEs 的溶出，故我们对其在海水环境中的溶出规律进行研究。

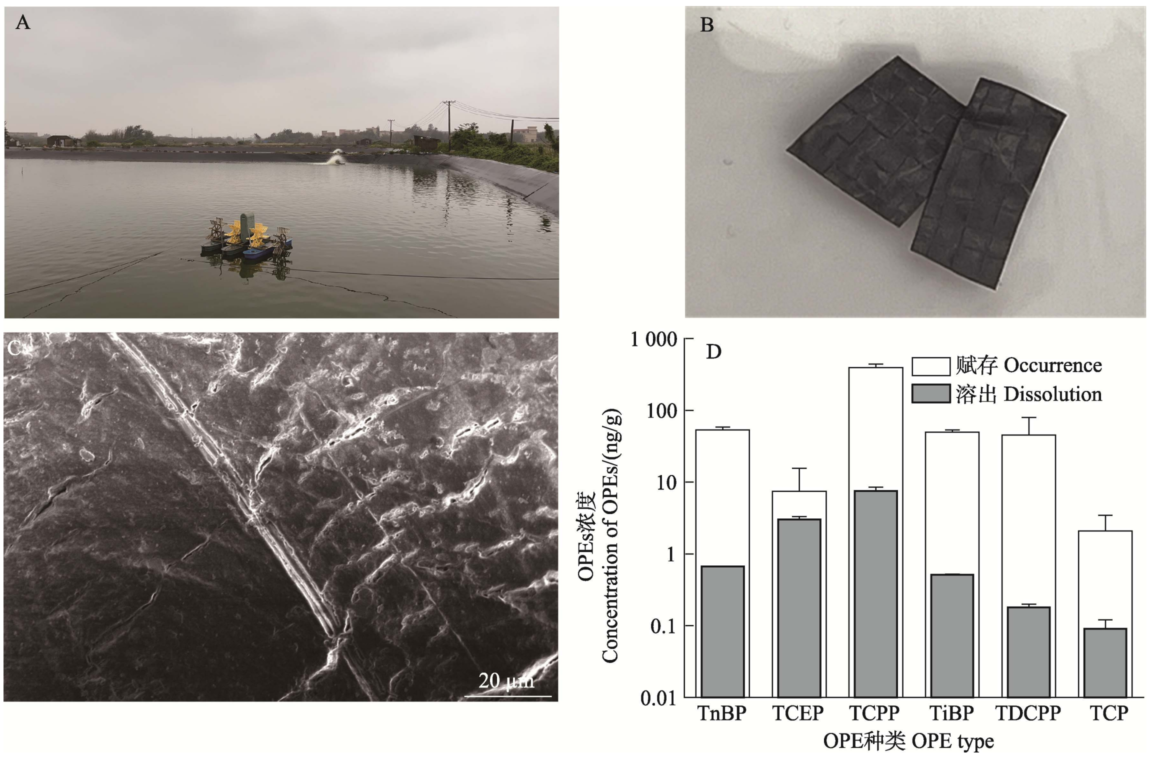

图 2 养殖用塑料防渗膜的采集及其 OPEs 的赋存和溶出

Fig.2 The collection of plastic impermeable membranes and the occurrence and dissolution of OPEs

a：采样现场照片；b：养殖用塑料照片；c：扫描电镜图；d：防渗膜中 OPEs 的赋存和溶出。

a: Sampling field photos; b: Aquaculture plastic photograph ; c: Scanning electron micrographs;
d: Occurrence and dissolution of OPEs in the impermeable film.

2.2　塑料防渗膜中 OPEs 的溶出规律

模拟溶出实验结果如图 2 所示，在 240 h 的实验中，氯代类 OPEs 溶出量最大，其中，TCPP 和 TCEP 分别达到(7.53±0.92) ng/g 和(3.02±0.28) ng/g，烷烃类 OPEs 溶出量大于芳香类 OPEs；而对于溶出率而言，氯代类 OPEs 溶出率最高，其中，TCEP 的溶出率达到 40.6%，这是由于 TCEP 的极性较高，且在海水中的溶解度较大。然而，烷烃类 OPEs 溶出率低于芳香类 OPEs，这可能是芳香类 OPEs 极性较弱，且具有较强的光降解性(Cristale *et al*, 2017)，导致其实际溶出率较低。

对 OPEs 的溶出量进行了多因素方差分析，结果表明，溶出量能被不同时间段、不同 OPEs 种类及二者的交互效应解释的部分有 97%。其中不同时间段和不同 OPEs 的种类对于溶出量均具有显著影响(P<0.001，P<0.05)。塑料防渗膜的动态溶出曲线如图 3 所示。其中，第 0~2 天的 OPEs 溶出速率最大，达到 0.69 ng/h，本研究采用的防渗膜是养殖鱼塘使用的旧膜，在野外已经老化，膜的表面粗糙，存在大量裂缝和孔隙(图 2c)，导致防渗膜中 OPEs 在该阶段大量溶出(图 3)。随后，在第 2~4 天内，塑料防渗膜中的 OPEs 溶出速率开始下降，为 0.3 ng/h，OPEs 溶出放缓；在第 4~6 天内，OPEs 溶出速率持续下降，为 0.1 ng/h；在第 6 天后，OPEs 的溶出开始达到平衡状态。可能在第 6 天时，膜表面原始存在的裂缝和孔隙中的 OPEs 几乎全部溶出，而达到防渗膜对 OPEs 释放和吸附行为的动态平衡。推测老化致使膜表面出现新的裂缝和孔隙，防渗膜中赋存的 OPEs 才能继续溶出。

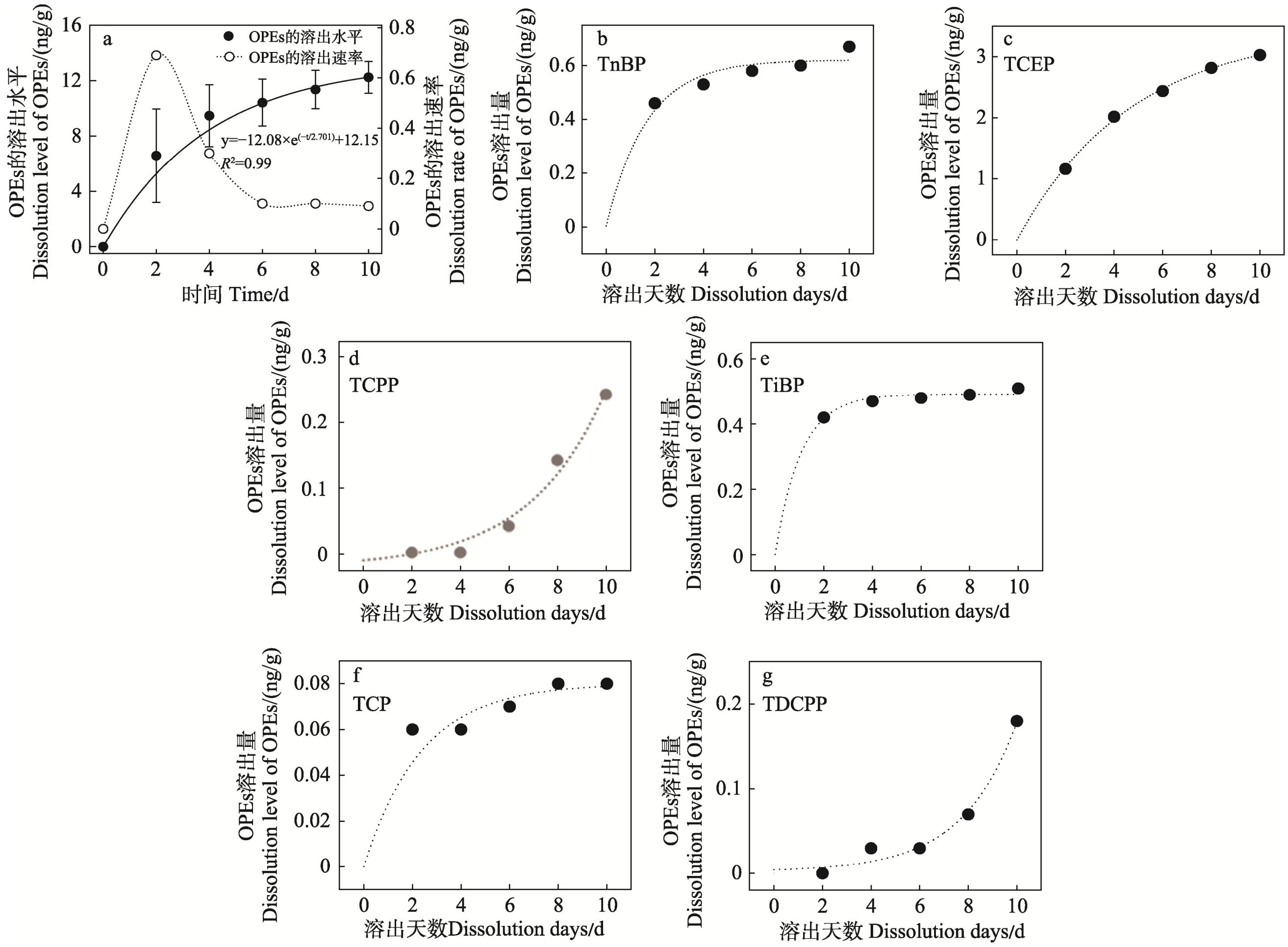

图 3　防渗膜中 OPEs 溶出水平及溶出速率
Fig.3　The dissolution level and dissolution rate of OPEs in the impermeable film

防渗膜中不同种类 OPEs 的溶出水平如图 3 所示，全过程溶出的 OPEs 种类有 TnBP、TCEP、TCPP、TiBP 和 TCP，其中以 TCPP 和 TCEP 的溶出量最多(图 4)；在这 6 种 OPEs 中，除 TDCPP 外，其他 OPEs 的溶出速率均随溶出时间增加而逐渐放缓达到平衡状态，这与 OPEs 的总体溶出趋势相似(图 3)，而

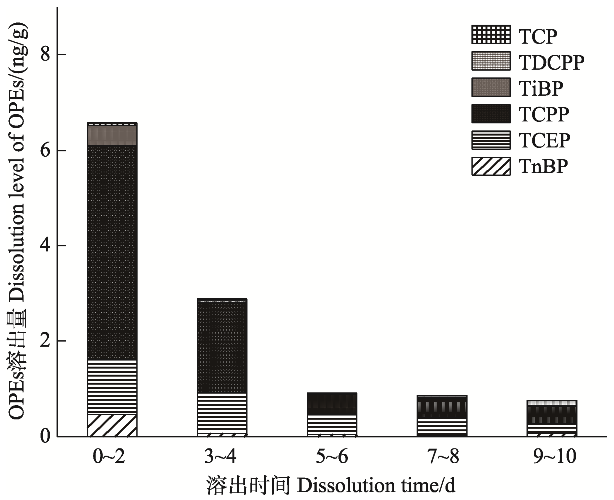

图 4 不同种类的 OPEs 在不同时间段的溶出量
Fig.4 Dissolution level of different kinds of OPEs in different periods

TDCPP 的溶出速率却随着时间增加而提高，但因其溶出水平较低，并未影响 OPEs 的总体溶出趋势。

2.3 塑料防渗膜中溶出 OPEs 在卤虫体内的生物富集

在卤虫暴露实验中，空白组卤虫的存活率为(94.00±0.02)%，防渗膜组卤虫的存活率为(91.00±0.04)%，存活率不具有显著差异性(P>0.05)，因此，防渗膜直接暴露的方式对卤虫生存率不造成影响。根据防渗膜的溶出实验结果，以实际养殖鱼塘中使用防渗膜面积为依据，将鱼塘防渗膜直接对卤虫进行暴露实验。如图 5 所示，在 48 h 的暴露后，卤虫体内总 OPEs 浓度为 159.18 ng/g，其中，TCPP 的浓度最高，达到(45.62±14.71) ng/g，其余依次为 TDCPP [(32.05±28.53 ng/g]、TiBP [(16.26±8.34) ng/g]和 TnBP [(15.41±3.54) ng/g]。TCP 浓度最低，仅有(7.15±0.33) ng/g。含氯类 OPEs (TCPP、TDCPP)因其生物难降解性而在生物体内的浓度较高(Bekele *et al*, 2021; Fu *et al*, 2020)，而芳香类 OPEs 比烷烃类 OPEs 更易被生物降解(Reemtsma *et al*, 2008; Lin *et al*, 2024; Wang *et al*, 2022)，因此，芳香类 OPEs (TCP)在生物体内的浓度最低。对比溶出种类发现，TCEP 未在卤虫体内检出，可能由于卤虫体内脂质含量极低，而 TCEP 较低的疏水性使其在卤虫体内的分配太低而无法检测到(Wang *et al*, 2019)。Bekele 等(2018)研究表明，较高的暴露浓度更有可能刺激生物体的代谢，从而降低生物积累的能力，由于 TCEP 的溶出量较高，可能刺激卤虫的代谢，因此，TCEP 在卤虫体内未检出。

根据公式(3)计算 OPEs 在卤虫体内的 BAF。从卤虫体内检测出的 5 种 OPEs 中，TCP 和 TDCPP 的 lgBAF 分别为 4.1 和 3.8，均大于 3.7，具有生物富集效应；TnBP 的 lgBAF 介于 3.3~3.7 之间，认为其具有潜在生物富集效应。由于 TCP 和 TDCPP 具有较高的辛醇-水分配系数，疏水性较强，因此，在卤虫体内容易富集(Bekele *et al*, 2018)。有趣的是，对比卤虫体内的 OPEs 浓度与 BAF 值(图 5)发现，尽管 TCPP 在卤虫体内的浓度最高，但并不存在生物富集效应；相反，TCP 在卤虫体内的浓度最低，却在卤虫体内表现出最强的生物富集效应。可能是由于 TCPP 具有较强的极性，更易在水中溶出，但不易在卤虫体内富集。与之相反，TCP 具有较弱的极性，在水中溶出率较低，但在卤虫体内富集程度更高。

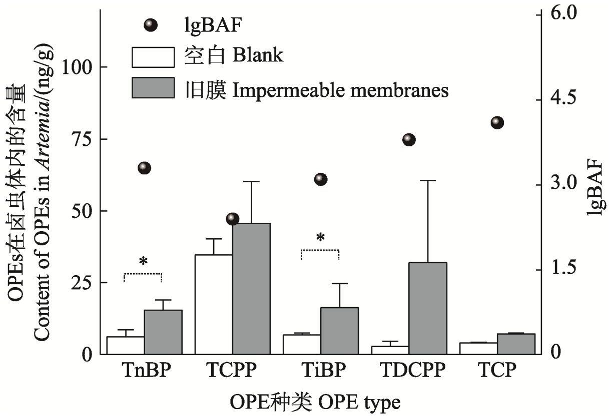

图 5 不同种类 OPEs 在卤虫体内的含量及其 lgBAF
Fig.5 The content and lgBAF of different types of OPEs in *Artemia*

3 总结

本研究通过实地采集养殖塘塑料防渗膜并进行溶出实验，发现共有 6 种 OPEs 溶出，主要以含氯类 OPEs 为主，且烷烃类 OPEs 溶出量大于芳香类 OPEs 溶出量。其中 TCPP 的溶出量最大，为(7.53±0.92) ng/g，TCP 溶出量最少；通过溶出率计算，含氯类 OPEs 的溶出率最高，而芳香类 OPEs 溶出率大于烷烃类 OPEs 溶出率。在第 0~2 天内，总 OPEs 的溶出速率最大，在第 6 天后，溶出速率开始趋于平衡。采用防渗膜对卤虫进行暴露实验，结果表明，防渗膜溶出的 OPEs 中，TCP、TDCPP 对卤虫具有明显的生物富集效应，TnBP 对卤虫具有潜在生物富集效应，而 TCPP 对卤虫不具有生物富集效应。在本研究中，通过采用防渗膜直接暴露的方式进行生物富集的研究，更清晰地阐明了 OPEs 从塑料进入环境再进入生物体中的实际转移过程，对生物体造成的生物富集效应更具有准确性。此外，应开展进一步的室内实验研究以及野外调查，

探明实际环境中 OPEs 对水产品的生物富集效应及其随食物链而产生的生物放大效应，从而准确评估养殖环境中 OPEs 的生态风险及健康风险。

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Release Behavior and Bioaccumulation Characteristics of Organophosphate Esters from Plastics in Marine Aquaculture

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Abstract Recently, the rapid development of the Chinese coastal economy and the expansion of aquaculture have led to an increased reliance on plastic materials within marine aquaculture systems. These materials, such as impermeable membranes, fishing nets, buoys, cages, and ropes, are extensively used for their beneficial properties. They are lightweight, durable, and cost-effective. However, the large-scale production and extensive use of plastics in aquaculture have increased concerns about their potential environmental impacts, particularly regarding the pollution of the marine environment and the associated risks to ecosystems. The primary concern is the plastic additives that are incorporated into these materials. These additives, including organophosphate esters (OPEs), are often physically mixed into the polymer matrices rather than chemically bonded. This physical integration increases their susceptibility to release into the surrounding environment through various processes, such as volatilization, leaching, abrasion, and dissolution, during the product's lifecycle. Despite these risks, the mechanisms and patterns of additive release, as well as the exposure risks presented to marine organisms, remain poorly understood.

This study focused explicitly on OPEs, a common group of plastic additives, to investigate their presence and behavior in plastic impermeable membranes used in marine aquaculture ponds. The study aimed to (1) identify the types and concentrations of OPEs present in the plastic impermeable membranes collected from marine aquaculture ponds, (2) simulate the dynamic dissolution of these OPEs in artificial seawater, and (3) evaluate the bioaccumulation potential of these OPEs in aquatic organisms, using *Artemia* as a model species.

We collected plastic impermeable membranes from wild marine aquaculture ponds and analyzed their OPE content using high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS). Our analysis revealed the presence of seven different types of OPEs, which included three aliphatic OPEs (TnBP and TiBP), one aromatic OPE (TCP), and three chlorinated OPEs (TCEP, TDCPP, and TCPP). TCPP was the most abundant, with a concentration of (395.15±48.05) ng/g, accounting for 63.12% of the total OPEs detected in the membranes. TnBP followed, exhibiting concentration of (52.96±5.25) ng/g. In contrast, TCP had the lowest concentration, contributing only 0.33% to the total OPEs.

To understand the dissolution behavior of OPEs in these membranes, we conducted a 240-h laboratory simulation. The impermeable membranes were submerged in artificial seawater with a salinity of 30, and water samples were collected every 48 h for analysis. The OPE concentrations in these water samples were determined using solid-phase extraction (SPE) followed by HPLC-MS/MS. At the end of the experiment, the total amount of OPEs dissolved from the membranes reached 12.24 ng/g. Chlorinated OPEs exhibited the highest dissolution rates, with TCEP showing a dissolution rate of

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40.6%. The general dissolution order was chlorinated OPEs > aromatic OPEs > aliphatic OPEs. Notably, the dissolution rate was highest during the first 48 h of the experiment and then gradually decreased over time. By approximately day 6, the dissolution rate reached a near-equilibrium state, likely due to the depletion of OPEs from cracks and pores on the membrane surface. At this stage, the membranes had likely reached a dynamic equilibrium between the release and adsorption of OPEs.

In addition to the dissolution experiments, we assessed the bioaccumulation potential of OPEs in *Artemia*, a species commonly used in marine studies. Plastic impermeable membranes were added to artificial seawater at concentrations that mimicked those typically found in marine aquaculture ponds. After exposure, *Artemia* and the surrounding water samples were collected, and the OPE concentrations were analyzed using ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS). Five OPEs—TCP, TDCPP, TnBP, TCPP, and TiBP—were detected in *Artemia*. We evaluated the degree of bioaccumulation using the bioaccumulation factor (BAF). The results indicated that TCP and TDCPP had significant bioaccumulation potential, with logBAF values greater than 3.7. TnBP exhibited a moderate bioaccumulation effect, with a logBAF between 3.3 and 3.7. However, TCPP and TiBP showed no significant bioaccumulation potential, as their logBAF values were below 3.3.

In conclusion, our study identified six distinct OPEs in the plastic impermeable membranes used in marine aquaculture, with chlorinated OPEs being the most prevalent. The results of the dissolution experiments revealed that OPEs are initially released rapidly from surface cracks and pores of the membranes, followed by a slower release as equilibrium is reached. Furthermore, the bioaccumulation experiments demonstrated that certain OPEs, particularly TCP and TDCPP, present bioaccumulation risks to marine organisms such as *Artemia*. These findings underscore the importance of managing plastic additives in marine aquaculture systems to mitigate the potential environmental impacts of plastic waste and its associated contaminants. The study provides valuable insights that can inform future strategies for reducing the ecological risks of plastic additives in marine environments.

Key words Aquaculture plastics; Organophosphate esters; Leaching behavior; Bioaccumulation