Universidade Federal do Rio Grande
Instituto de Ciências Biológicas
Pós-graduação em Biologia de Ambientes Aquáticos Continentais

Análise de ocorrência de contaminantes emergentes da Lagoa Mirim e efeitos do inseticida imidacloprido em espécies do zooplâncton

Karen Pinheiro Lackman

Orientadora: Profª. Drª. Raquel Aparecida Moreira
Co-orientadora: Profª. Drª. Camila de Martinez Gaspar Martins

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ATA DE DEFESA DE DISSERTAÇÃO DE MESTRADO EM BIOLOGIA DE AMBIENTES AQUÁTICOS CONTINENTAIS– Nº 006/2026

Às 9:00h (nove horas) do dia 24 (vinte e quatro) do mês de junho de 2026 (dois mil e vinte e seis), no Laboratório de Bioinformática do ICB e via Webconferêcia (https://conferenciaweb.rnp.br/sala/bioinformatica-icb-furg) reuniram-se docentes, discentes e comunidade em geral, para a defesa pública da Dissertação de Mestrado da acadêmica **Karen Pinheiro Lackman**. A Dissertação intitulada **"Análise de ocorrência de contaminantes emergentes da Lagoa Mirim e efeitos do inseticida imidacloprido em espécies do zooplâncton"** foi avaliada pela Banca Examinadora composta pela Profa. Dra. Raquel Aparecida Moreira (orientadora, PPGBAC/USP), Profa. Dra. Camila de Martinez Gaspar Martins (coorientadora, PPGBAC/FURG), Dra. Fernanda Chaves Lopes (PPGBAC/FURG) e Dra. Mariana Vellosa Capparelli (Instituto IMDEA Água). Após a defesa e arguição pública, a Banca Examinadora reuniu-se, para deliberação final, e considerou a acadêmica **APROVADA**. Desta forma, a acadêmica concluiu mais uma das etapas necessárias para a obtenção do grau de **MESTRE EM BIOLOGIA DE AMBIENTES AQUÁTICOS CONTINENTAIS**. Nada mais havendo a tratar, às 12:00h (doze horas) foi lavrada a presente ATA, que lida e aprovada, foi assinada pelos membros da Banca Examinadora, pela Acadêmica e pela Coordenadora do Curso.

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RESUMO

Os contaminantes de preocupação emergente representam uma ameaça crescente aos ecossistemas aquáticos, especialmente em regiões influenciadas por atividades agrícolas e urbanas. Esta dissertação teve como objetivo analisar a ocorrência de contaminantes ambientais em águas superficiais da bacia hidrográfica da Lagoa Mirim, sul do Brasil, e avaliar, em laboratório, os efeitos do inseticida imidacloprido em espécies zooplanctônicas. No primeiro capítulo, foram analisadas amostras de água coletadas em seis pontos da Lagoa Mirim, em quatro períodos associados ao ciclo do arroz irrigado, além da realização de uma revisão sistemática da literatura sobre qualidade da água e contaminantes na região entre 2001 e 2025. Dos 26 compostos investigados, 22 foram detectados, incluindo herbicidas, inseticidas, fungicidas, metabólitos de herbicidas, cafeína e um antibiótico. Tebuconazol, 2,4-D, cafeína, tiametoxam e imidacloprido apresentaram as maiores concentrações. A presença de compostos também na entressafra indica a persistência ou múltiplas fontes de entrada desses contaminantes, enquanto a revisão evidenciou escassez de estudos sobre contaminantes emergentes na bacia. No segundo capítulo, o imidacloprido (um dos compostos detectados na Lagoa Mirim) foi avaliado em testes agudos, crônicos e de alimentação com *Daphnia magna*, *D. similis*, *Ceriodaphnia dubia* e *C. silvestrii* (espécie nativa). Os resultados demonstraram diferenças interespecíficas de sensibilidade, com maior toxicidade aguda para *C. silvestrii*, seguida por *C. dubia*, *D. similis* e *D. magna*. A exposição crônica reduziu a reprodução de *D. similis* e *D. magna* a partir de 0,025 mg/L, e *C. silvestrii* apresentou redução da taxa de ingestão em 0,1 mg/L. De forma integrada, os resultados demonstram a ocorrência ampla de contaminantes na Lagoa Mirim e indicam que o imidacloprido pode causar efeitos letais e subletais em organismos zooplanctônicos, reforçando a importância do monitoramento ambiental e da inclusão de espécies nativas em avaliações de risco ecológico.

Palavras-chave: Agrotóxico; Avaliação de risco ecológico; Bacia hidrográfica transfronteiriça; Cladóceros; Qualidade da água.

ABSTRACT

Contaminants of emerging concern represent a growing threat to aquatic ecosystems, especially in regions influenced by agricultural and urban activities. This dissertation aimed to analyze the occurrence of environmental contaminants in surface waters of the Mirim Lagoon watershed, southern Brazil, and to evaluate, under laboratory conditions, the effects of the insecticide imidacloprid on zooplankton species. In the first chapter, water samples collected from six sites in Mirim Lagoon were analyzed during four periods associated with the irrigated rice cycle, together with a systematic literature review on water quality and contaminants in the region between 2001 and 2025. Of the 26 compounds investigated, 22 were detected, including herbicides, insecticides, fungicides, herbicide metabolites, caffeine, and an antibiotic. Tebuconazole, 2,4-D, caffeine, thiamethoxam, and imidacloprid showed the highest concentrations. The presence of compounds also during the off-season indicates persistence or multiple input sources of these contaminants, while the review highlighted the scarcity of studies on emerging contaminants in the watershed. In the second chapter, imidacloprid, one of the compounds detected in Mirim Lagoon, was evaluated in acute, chronic, and feeding assays with *Daphnia magna*, *D. similis*, *Ceriodaphnia dubia*, and *C. silvestrii* (a native species). The results demonstrated interspecific differences in sensitivity, with greater acute toxicity for *C. silvestrii*, followed by *C. dubia*, *D. similis*, and *D. magna*. Chronic exposure reduced reproduction in *D. similis* and *D. magna* from 0.025 mg/L, and *C. silvestrii* showed a reduction in ingestion rate at 0.1 mg/L. Overall, the results demonstrate the widespread occurrence of contaminants in Mirim Lagoon and indicate that imidacloprid can cause lethal and sublethal effects in zooplankton organisms, reinforcing the importance of environmental monitoring and the inclusion of native species in ecological risk assessments.

Key-words: Pesticide; Ecological risk assessment; Transboundary watershed; Cladocerans; Water quality.

APRESENTAÇÃO

Esta dissertação contém uma introdução geral, objetivo geral e específicos, referências bibliográficas e a apresentação de dois capítulos. Ambos capítulos estão em formato de artigo científico, redigido em inglês e de acordo com as normas das revistas a quais pretende-se submeter os trabalhos.

No primeiro capítulo, avaliamos a ocorrência de contaminantes ambientais em seis pontos da lagoa Mirim, amostrados em quatro períodos associados ao ciclo do arroz irrigado, integrando essas amostragens com uma revisão sistemática da literatura publicada entre 2001 e 2025 sobre contaminantes emergentes, qualidade da água, agrotóxicos, metais pesados, fármacos e microplásticos na Bacia Hidrográfica da Lagoa Mirim. O mesmo está intitulado como Environmental contaminants in a strategic transboundary watershed: a systematic review and occurrence assessment in Lagoa Mirim (Southern Brazil) e será submetido para a revista *Environmental Monitoring and Assessment*.

O segundo capítulo aprofunda a avaliação dos possíveis efeitos ecológicos de um dos compostos detectados na Lagoa Mirim, o imidacloprido. Para isso, foram realizados ensaios laboratoriais com espécies zooplanctônicas de cladóceros, avaliando efeitos agudos, crônicos e subletais, como sobrevivência, reprodução e taxa de ingestão alimentar. Essa abordagem permite conectar a ocorrência ambiental observada no primeiro capítulo com efeitos ecotoxicológicos em organismos aquáticos, contribuindo para uma avaliação mais integrada do risco ecológico associado a esse inseticida. Este está intitulado como “Species-specific sensitivity to imidacloprid: ecotoxicological effects on congeneric cladoceran and ecological risk assessment”, e que foi submetido para a revista *Ecotoxicology*.

Ao final são apresentadas as considerações finais e perspectivas do estudo.

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INTRODUÇÃO GERAL

A água doce é um dos recursos mais essenciais do planeta, sendo vital para o desenvolvimento humano e para a manutenção da vida selvagem (Sajid et al., 2018). No entanto, a industrialização e o crescimento populacional têm contribuído para a degradação desses recursos, tornando cada vez mais desafiador o fornecimento de água potável e segura em escala global (Nasrollahzadeh et al., 2021). Os contaminantes podem atingir os corpos hídricos por meio da descarga de águas residuais não tratadas ou ainda tratadas, mas sem a remoção completa dessas substâncias (Nasrollahzadeh et al., 2021).

As fontes de poluição da água podem ser classificadas como pontuais ou não pontuais. As fontes pontuais correspondem às descargas diretas de contaminantes em rios, lagos e oceanos com origem definida, como redes de esgoto doméstico, efluentes industriais, derramamentos acidentais, atividades de mineração e transbordamentos associados a eventos de tempestade. Tornando-as mais fáceis de monitorar e regular em comparação com as fontes não pontuais. As fontes não pontuais resultam de descargas difusas antes de atingirem os cursos d'água, podendo variar significativamente no tempo e no espaço. Como exemplos destacam-se as práticas agrícolas, habitações dispersas, deposição atmosférica, obras de construção civil, escoamento superficial do solo e transporte fluvial (Holt, 2000). As práticas agrícolas, por exemplo, introduzem de forma significativa (através do escoamento) fertilizantes, agrotóxicos e dejetos de animais que possuem nutrientes como nitrogênio (N) e fósforo (P), o que pode levar à eutrofização e ao crescimento de florações de algas nocivas (Singh et al., 2020).

A poluição hídrica ocorre quando há aumento na concentração de determinadas substâncias, resultando em impactos negativos tanto para os organismos aquáticos quanto para os seres humanos. Entre as fontes dessa poluição destacam-se substâncias de origem natural, como compostos liberados por processos biogeoquímicos ou pela excreção de organismos, além de poluentes como óxidos, metais pesados, nitrogênio, hidrocarbonetos e radiação. Por outro lado, existem substâncias que não ocorrem de forma natural, ou seja, não ocorrem na natureza e são originados pelo homem. Entre elas destacam-se agrotóxicos, surfactantes e compostos petroquímicos, que podem ser liberados por efluentes domésticos, agrícolas e industriais e sofrer processos de degradação no ambiente, originando novos produtos químicos potencialmente mais persistentes ou tóxicos (Manasa e Mehta, 2020; Sahoo e Goswami, 2024). A Figura 1, ilustra as fontes de poluição da água como pontuais ou não pontuais e os elementos do ciclo hidrológico.



Figura 1. Ilustração de fontes difusas e pontuais de poluição da água, associadas a elementos do ciclo hidrológico. **Fonte:** traduzido e adaptado de EPA, Office of Water, Nonpoint Source Program (2024).

A presença desses contaminantes compromete a disponibilidade de água adequada tanto para o consumo humano quanto para a manutenção dos ecossistemas aquáticos (lin et al., 2022). Alguns poluentes químicos podem causar sérios danos à saúde humana, enquanto muitos outros apresentam efeitos de longo prazo ainda pouco compreendidos. O relatório *National Lakes Assessment* (2022) indicou que apenas 16% dos lagos avaliados nos Estados Unidos estavam em boas condições, com base em medidas de perturbação das margens, indicando níveis moderados a altos de atividade humana e alterações na linha costeira em 84% dos lagos. Ainda, alguns contaminantes estavam presentes em todos os tecidos dos peixes (EPA, 2024).

No Brasil, os piores indicadores de qualidade da água concentram-se em áreas urbanizadas, principalmente devido ao lançamento de esgotos domésticos e à intensa ocupação do solo, enquanto regiões menos antropizadas apresentam melhor qualidade (ANA, 2025). Além disso, estudos demonstram a ocorrência de contaminantes emergentes em ambientes aquáticos, incluindo águas superficiais, subterrâneas, potáveis e residuárias. Esses compostos abrangem, produtos farmacêuticos, agrotóxicos e compostos industriais (Montagner et al., 2019; Santos et al., 2024). Essas substâncias foram detectadas tanto em águas superficiais quanto subterrâneas, de fontes urbanas e agrícolas, representando riscos potenciais para os organismos aquáticos e para a saúde humana.

Contaminantes emergentes

Nas últimas décadas, houve um aumento notável na constatação de diversos tipos de micropoluentes orgânicos provenientes de atividades humanas nos ecossistemas aquáticos. Isso se reflete tanto no aumento do número de substâncias identificadas como nas concentrações detectadas (Wilkinson et al., 2022). Muitas dessas substâncias não são necessariamente novas, mas devido principalmente às limitações da instrumentação analítica no passado, não eram detectadas. Com o avanço da capacidade analítica e o aprimoramento das técnicas de extração e detecção, tornou-se possível realizar análises de compostos com diferentes características físicas e químicas em diversas amostras de ecossistemas aquáticos continentais (Richardson e Ternes, 2022). Dos diferentes tipos de poluentes, alguns são considerados contaminantes emergentes, que podem ser definidos como "poluentes que atualmente não estão incluídos nos programas de monitoramento de rotina e que podem ser candidatos a regulamentação futura, dependendo de pesquisas sobre sua (eco) toxicidade, efeitos potenciais à saúde e percepção do público e no monitoramento de dados relativos à sua ocorrência nos vários compartimentos ambientais" de acordo com Usepa (2008) e Norman (2024).

Alguns exemplos de contaminantes emergentes são os produtos de beleza e higiene pessoal, fármacos, hormônios, agrotóxicos, microplásticos, solventes, retardadores de chamas, alguns metais, compostos de uso industrial (bifenilos policlorados - PCBs, bisfenol, ftalato e organotinas), entre outros (Reichert et al., 2019; Unesco, 2021). A preocupação com esses contaminantes se deve ao fato de que devido ao amplo uso dessas substâncias nas atividades diárias em grande parte da população, sua presença tem sido frequentemente detectada em água, sedimentos, solos, atmosfera, plantas, organismos vivos, produtos alimentícios e espécies protegidas, ou ainda em locais onde não se tem atividade antropogênica (Routti et al. 2019; Galindo- Miranda *et al*., 2019; Deblonde *et al*., 2011), demonstrando seu transporte desenfreado em escala global. Diversos pesquisadores, em diferentes partes do mundo, estão documentando a presença, a ocorrência, o transporte e o impacto desses contaminantes emergentes nos recursos hídricos (Xabadia et al. 202; Richardson et al. 2026; Li et al. 2024; Wang et al. 2024).

Os contaminantes emergentes estão amplamente distribuídos nos ambientes aquáticos em escala global, com registros em países, como por exemplo, China, Portugal, México, Colômbia e Brasil. A presença de fármacos, hormônios, cosméticos, bactérias resistentes a antibióticos e agrotóxicos tem sido constatada em rios, lagos e outros corpos d'água de todos os continentes. Essa situação decorre, principalmente, do lançamento de efluentes urbanos, hospitalares, industriais e agrícolas, visto que somente 51,8% do volume de esgoto gerado no Brasil é tratado (Ministério das Cidades, 2025), aliado à limitação dos processos convencionais utilizados nas estações de tratamento de esgoto, que não conseguem remover esses compostos de forma eficaz (Morin-Crini et al., 2022). E, em algumas regiões do Brasil, nem mesmo

são estudadas sua ocorrência (Ribas et al., 2021; Montagner; Vidal; Acayaba, 2017, Quadra et al., 2017, Petrie et al., 2015). Nesse contexto, a adoção de tecnologias mais modernas, como sistemas de tratamento terciário, é apontada como uma medida fundamental para diminuir a entrada desses poluentes nos ecossistemas aquáticos (Morin-Crini et al., 2022).

A detecção de contaminantes emergentes (CEs) apresenta uma grande limitação devido à natureza complexa dessas substâncias, a misturas de vários contaminantes, a persistência e bioatividade em baixas concentrações e a falta de métodos de detecção padronizados. O monitoramento e o avanço de técnicas analíticas são necessários para a identificação desses contaminantes em níveis residuais no meio ambiente para que se possa proteger tanto a saúde pública como a dos ecossistemas (Li et al., 2024).

Efeitos dos contaminantes emergentes sobre organismos aquáticos

Além da presença desses contaminantes em ecossistemas aquáticos, diversos estudos relatam os efeitos que esses compostos podem causar em organismos não-alvo e nos sistemas biológicos desses organismos pertencentes a diferentes níveis tróficos. Entre os resultados observados estão alterações fisiológicas, reprodutivas, genéticas e morfológicas após a exposição a estes contaminantes (Iturburu et al., 2017; Sumon et al., 2018). Nesse contexto, esses contaminantes prejudiciais, em conjunto com fatores de estresse naturais, podem intensificar os impactos sobre a biota, afetando processos ecológicos e interações biológicas dentro dos ecossistemas, o que pode levar a danos irreversíveis nas cadeias tróficas (Castro et al., 2020).

Com isso, se tem a necessidade de analisar os efeitos desses contaminantes em organismos aquáticos, como, por exemplo, os microcrustáceos (Leite et al., 2022). Os mesmos possuem um papel importante na cadeia alimentar aquática, são consumidores primários, servindo de alimento para indivíduos maiores (Kadam e Agrawal, 2015), como peixes e insetos. Quando esses organismos são afetados devido ao seu nível de sensibilidade, os mesmos podem gerar reações e alterações no desempenho de várias outras espécies nessa estrutura trófica (Hayashi et al., 2020). Alguns fatores como a disponibilidade de alimentos e elementos químicos específicos dissolvidos na água (Carvalho e Bonecker, 2016), fenômenos naturais como a chuva que podem ocasionar mudanças na turbidez e assoreamento no meio (Adámek et al., 2016) e ações antrópicas que podem causar impactos tanto diretos como indiretos, podem comprometer o desenvolvimento desses indivíduos (Loureiro et al., 2011).

Nos ambientes aquáticos de água doce, os ensaios toxicológicos surgem como uma importante ferramenta para avaliar o impacto na cadeia trófica decorrente da exposição biológica desses contaminantes (Pompêo et al., 2022). As espécies zooplanctônicas, como as do gênero *Daphnia* são usualmente empregadas

como bioindicadores de qualidade ambiental, devido às rápidas respostas às alterações ambientais (Smirnov, 2017). Durante esses ensaios, são observadas possíveis manifestações biológicas nos organismos estudados, como imobilidade, inibição de crescimento e alterações reprodutivas, entre outras (Prósperi, 1993). Ainda, estes invertebrados possuem o potencial de transferência desses contaminantes para níveis tróficos superiores por se encontrarem na base da cadeia alimentar (Battuello et al., 2016).

Os gêneros *Daphnia* e *Ceriodaphnia* são os cladóceros mais utilizados em estudos de ensaios toxicológicos (Ghazy et al., 2011). Dentro desses gêneros, se destacam duas espécies exóticas internacionalmente padronizadas e que são amplamente utilizadas em testes laboratoriais sendo a *Daphnia magna* que têm larga distribuição no hemisfério norte (ABNT NBR 12.713, 2016) e *Ceriodaphnia dubia* que são encontrados na Europa e na América do Norte (ABNT NBR 13. 373, 2022). A *D. magna* é um microcrustáceo, conhecido como pulga-d'água, que varia de 5 mm a 6 mm de comprimento, atua como consumidor primário na cadeia alimentar aquática e se alimenta por filtração de material orgânico particulado em suspensão. A *C. dubia* é um microcrustáceo de 0,8 a 0,9 mm de comprimento, de corpo ovalado e com 8 a 10 espinhos anais. Também conhecidos como pulgas-d'água, são consumidores primários da cadeia alimentar de ambientes de água doce e alimentam-se por filtração de material orgânico particulado (ABNT NBR 13. 373, 2022).

A *D. similis* também é um cladócero exótico que vive em águas continentais da Europa e Ásia (principalmente), com comprimento máximo de 3,5 mm (Hudec, 1991). Estes apresentam uma alta sensibilidade a contaminantes aquáticos, possuem fácil cultivo em laboratório, a reprodução é assexuada (Buratini, Bertoletti, Zagatto, 2004), ciclo de vida curto e consistência reprodutiva (Jeyavani et al., 2023). São amplamente utilizados em ensaios de ecotoxicidade devido à sua sensibilidade às variações ambientais, ao seu hábito alimentar baseado em filtração e ao seu modo de reprodução por partenogênese. Além disso, esses organismos estão distribuídos em larga escala em regiões de clima temperado (Jeyavani et al., 2023).

Muitos esforços estão sendo feitos para a utilização de espécies nativas de clima tropical já que as mesmas apresentam elevada sensibilidade e representam o local onde habitam (Moreira et al., 2014). Um exemplo é a *C. silvestri* que é uma espécie tropical que pode ser encontrada na América do Sul como nos estados de São Paulo, Rio Grande do Sul, Goiás e Distrito Federal (Matsumura-Tundisi & Tundisi, 2011), é de fácil cultivo em laboratório e com ciclo de vida curto (ABNT, 2022). Apresenta uma alta sensibilidade a impactos de origem antrópica, como a contaminação por agrotóxicos (Robles-Vargas, 2015). Essa espécie apresenta rápidas respostas nos testes crônicos, podendo ser realizado em oito dias (Hayasaka et al., 2012, além de ser extremamente pequena e ser mais sensível que *C. dubia*, espécie exótica (Silva; Daam; Gusmão, 2020). As quatro espécies zooplanctônicas citadas anteriormente podem ser observadas na Figura 2.

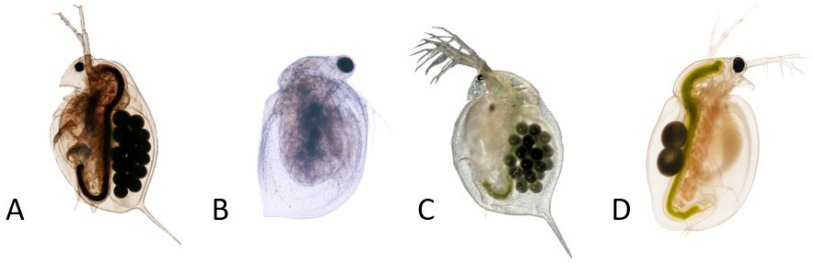


Figura 2. Ilustração de *Daphnia similis* (A), *Ceriodaphnia silvestrii* (B), *D. magna* (C) e (D) *C. dubia*.

Agrotóxicos em ambientes aquáticos

No Brasil, o agronegócio desempenha papel significativo na economia: em 2024, as exportações do setor atingiram US$ 164,4 bilhões, correspondendo a 49% das exportações totais do país (Brasil, 2025). No mesmo ano, o agronegócio representou aproximadamente 22% do Produto Interno Bruto (PIB) brasileiro, se destacando globalmente entre os principais fornecedores de alimentos. A China, União Europeia, Estados Unidos e África foram os principais destinos das exportações brasileiras (Cepea, 2025).

Entretanto, as práticas agrícolas utilizam elevadas aplicações de agrotóxicos em seus cultivos (Gaboardi, Candiotto, Panis, 2023). Em 2025, o Brasil concedeu o registro de 912 produtos de agrotóxicos, componentes e afins (MAPA, 2025). Com a elevada utilização desses produtos, os agrotóxicos são carreados e detectados nos ecossistemas aquáticos continentais, por meio do escoamento superficial, carreamento, lixiviação e infiltração (Acayaba et al., 2021). Ao atingir o ambiente, podem causar toxicidade aos organismos aquáticos, aos animais terrestres e aos humanos (Andrade Palma et al., 2011).

Estudos realizados no Brasil demonstraram a ocorrência de agrotóxicos em ambientes aquáticos. Nas regiões sul, um número significativo de agrotóxicos foi detectado em águas superficiais, com dezenas de compostos identificados em reservatórios de abastecimento de água (Peresin et al., 2023). Da mesma forma, na região amazônica, múltiplas classes de agrotóxicos, incluindo inseticidas, herbicidas e fungicidas, foram relatadas em sistemas de água doce (Rico et al., 2022). No estado de São Paulo, estudos de monitoramento de longo prazo também revelaram a presença de diversos resíduos dessas moléculas em amostras de água (Montagner et al., 2019). A Figura 3, ilustra as formas de entrada dos agrotóxicos no meio ambiente.



Figura 3. Vias de entrada dos agrotóxicos no ambiente aquático e mobilização a partir do solo. Fonte: Dores e De-Lamonica-Freire (1999), modificado de Solomon (1992).

Dentre os agrotóxicos amplamente utilizados no Brasil, o imidacloprido ($C_9H_{10}ClN_5O_2$) (IMD) se destaca, devido a sua ampla comercialização e utilização (Brasil, 2025). Foi o primeiro a ser comercializado na década de 90 nos EUA e hoje é um dos mais utilizados no mundo (Xia et al., 2016). Ainda que a sua utilização tenha sido proibida em algumas localidades, como na Europa, o inseticida segue sendo muito utilizado no combate às pragas em muitas regiões (European Commission, 2018; Wang et al., 2023).

É utilizado no Brasil desde 1994 e possui autorização de uso em mais de 40 culturas, incluindo soja, milho, trigo, algodão, café, cana-de-açúcar, citros e hortaliças (IBAMA, 2019). Com uma classificação toxicológica de classe II (Altamente tóxico) e de periculosidade ambiental de classe II (Produto muito perigoso ao meio ambiente), seu uso é regulamentado e amplamente adotado no Brasil (Brasil, 2025). A reavaliação ambiental do ingrediente ativo foi finalizada pelo Ibama em 2021, em razão de seus efeitos sobre abelhas, resultando em medidas de mitigação de risco para produtos contendo imidacloprido (IBAMA, 2021). Com isso, foram estabelecidas medidas de mitigação, incluindo a restrição ou exclusão de determinados usos, alterações em rótulos e bulas e exigências de práticas destinadas a reduzir a exposição de polinizadores.

Esse composto é utilizado tanto no setor agropecuário quanto no uso farmacêutico em animais, sendo empregado como inseticida para tratamento do solo, sementes e folhas em diversas culturas, incluindo cereais, algodão, frutas, batata, arroz, bebida sacarina, milho, grama e hortaliças (AGROFIT, 2025). É um inseticida neonicotinóide (inseticidas estruturalmente semelhantes a nicotina), que causa a morte dos insetos após ser ingerido ou ao entrar em contato, afetando o sistema nervoso ao bloquear os receptores pós-

sinápticos da acetilcolina (Tomizawa et al., 2005). Seu mecanismo de ação se dá por um estímulo contínuo da mensagem da acetilcolina no sistema, o que leva à uma estimulação contínua e disfunção do sistema nervoso causando a inibição da neurotransmissão dos insetos, paralisia e, eventualmente, a morte (Ma et al., 2021). Seu modo de ação age semelhante para organismos aquáticos, pois interfere nos sítio de ligação da acetilcolina localizado no domínio extracelular (Malhotra et al., 2021). É considerado muito tóxico para a vida aquática, tanto para risco agudo como para crônico (NCBI, 2026). O inseticida imidacloprido pode ser encontrado no mercado em formatos de cristais incolores ou na forma de pó bege. Possui solubilidade em água de 610 mg/L a 20 °C e um coeficiente de partição octanol-água (Kow) = 0.57 a 21 °C. É fotodegradado na água e no solo em horas e meses, respectivamente - suscetível à fotólise direta pela luz solar. O seu tempo de meia-vida é de 1 a 10 dias em água, e na ausência de luz, sua degradação pode variar de 30-150 dias e sua degradação total no meio aquático varia de 14-30 dias. No solo, a sua mobilidade é de moderada a baixa com base no Coeficiente de Sorção normalizado pelo Carbono Orgânico (Koc) de 156 a 800 (NCBI, 2026).

Por possuir uma alta solubilidade e uma meia-vida longa na água (Morrissey et al., 2015), a poluição de corpos d'água superficiais pelo inseticida, é identificada como um grande obstáculo enfrentado para a conservação dos recursos hídricos, especialmente em bacias próximas a regiões agrícolas (Deknock et al., 2019). O imidacloprido foi detectado em todas as amostras investigadas em águas superficiais de Ontário, Canadá (8 locais), sendo o nível mais alto de ocorrência entre os outros neonicotinoides estudados. As concentrações variaram entre 0,0067 e 0,585 $\mu g\ L^{-1}$. Em Lebo Drain e Sturgeon Creek, aproximadamente 75% das amostras continham imidacloprido em concentrações que excediam o valor da diretriz do Canadian Council of Ministers of the Environment (CCME) (0,230 $\mu g\ L^{-1}$) (Struger et al., 2017).

Na California – EUA, um dos inseticidas mais frequentemente detectados nas três áreas de águas superficiais urbanas estudadas foi o IMD (0,05 – 0,160 $\mu g\ L^{-1}$) entre os anos de 2008 e 2011 (Ensminger et al., 2013). Ainda no mesmo estado, Batikian et al. (2019) em seu estudo detectou uma frequência de detecção do imidacloprido em 100% das amostras de água da superfície de Forester Creek com uma concentração que variou de 0,0038 a 0,096 $\mu g\ L^{-1}$. Mais de 60% das amostras excederam o parâmetro de exposição crônica da U.S. Environmental Protection Agency - US EPA (2025) (10 µg/L). No distrito de Wujin (noroeste do lago Taihu), província de Jiangsu, China, a taxa de detecção do imidacloprido foi de 88% com uma concentração máxima de 0,438 $\mu g\ L^{-1}$ em águas superficiais (lagos, rios principais e afluentes) (Zhou et al., 2020). Em São Paulo, região com a maior produção de cana-de-açúcar do mundo, o imidacloprido foi encontrado nas maiores concentrações em águas superficiais com uma faixa de concentração que variou entre 0,0067 – 2,579 $\mu g\ L^{-1}$ (Acayaba et al., 2021). A contaminação por imidacloprido em diferentes locais é preocupante devido aos efeitos tóxicos que esse inseticida pode causar em organismos aquáticos. Com isso, avaliar os efeitos desse inseticida neonicotinóide nos ecossistemas de água doce brasileiros se torna de extrema importância (Queiroz et al., 2022).

De acordo com a literatura, o imidacloprido pode afetar diferentes níveis tróficos. Lozano et al. (2025) avaliaram os efeitos do imidacloprido sobre algas e observaram que baixas concentrações podem promover crescimento algal na ausência de zooplâncton, indicando possíveis efeitos indiretos ou alterações na dinâmica trófica em ambientes aquáticos contaminados. Também foram observados efeitos tóxicos nas populações e comunidades de zooplâncton e macroinvertebrados da Amazônia equatoriana por Cabrera et al (2024). O estudo mostrou alta sensibilidade dos invertebrados tropicais, com efeitos sobre a estrutura das comunidades em mesocosmos (Cabrera et al., 2024). Liu et al. (2025) avaliaram respostas de biomarcadores de estresse oxidativo e neurotoxicidade em três organismos marinhos: o misídeo *Neomysis awatschensis*, o peixe *Oryzias melastigma* e o molusco bivalve *Perinereis aibuhitensis.* Os resultados demonstraram que o estresse oxidativo e os biomarcadores neurotóxicos dos diferentes organismos apresentaram tendências distintas com o aumento da concentração de IMI, com danos na peroxidação lipídica (LPO). Efeitos também foram observados em anfíbios, Velásquez e Bautista (2025) testaram a toxicidade aguda do imidacloprido e do 2,4-D em girinos de duas espécies tropicais de anuros (*Boana platanera* e *Engystomops pustulosus*). O inseticida IMD levou a uma redução no comprimento total dos girinos de *B. platanera* e induziu imobilidade total nos indivíduos sobreviventes de ambas as espécies.

Esses resultados reforçam a necessidade de avaliar o imidacloprido não apenas por meio de testes padronizados, mas também por abordagens que incluam diferentes níveis tróficos e espécies nativas, especialmente em ecossistemas tropicais de água doce.

Monitoramento de Contaminantes Emergentes nas águas da Lagoa Mirim

A bacia hidrográfica da Lagoa Mirim localizada entre o estado do RS - no extremo sul do Brasil e Uruguai, possui uma superfície aproximada de 62.250 km², dividida entre o território brasileiro (53%) e o uruguaio (47%). A área estabelece uma das principais bacias hidrográficas do Rio Grande do Sul, formando o maior complexo lagunar da América do Sul juntamente com a Laguna dos Patos (Silva et al., 2024). A Lagoa Mirim e as áreas úmidas ao redor estão entre as coordenadas geográficas de 31°30' a 34°35' de latitude Sul e 53°31' a 55°15' de longitude Oeste. Constitui um importante sistema na América do Sul, desempenhando papéis tanto ecológicos como econômicos relacionados à agricultura para o estado do Rio Grande do Sul e para o Uruguai (Oliveira et al., 2015). O clima na região é caracterizado como subtropical de verão úmido e quente, isto indica temperaturas médias superiores a 22°C nos meses mais quentes e inferiores a 18°C nos meses mais frios, com uma média anual de precipitação pluvial de 1.450 mm (Alvares et al., 2013).

A biodiversidade da bacia é de extrema importância para a conservação das paisagens e ecossistemas, sendo: a faixa costeira do Atlântico com lagoas e lagunas nos dois países; várias zonas baixas e úmidas associadas a lagoas e florestas com uma rica biodiversidade; Bioma Pampa e matas ciliares e úmidas; e terras altas associadas com o sistema das Serras de Sudeste (Cordeiro e Hasenack, 2009). As áreas úmidas possuem um papel fundamental devido à riqueza de fauna e flora que abrigam o local, além de servirem como refúgio para aves migratórias. Também desempenham funções essenciais na regulação do fluxo dos rios, no controle de enchentes, recarga de aquíferos e no aprimoramento da qualidade da água. Ainda, possui grande relevância sociocultural, sendo valorizada por suas belezas cênicas e paisagísticas (MMA, 2000).

No território Uruguaio, o governo reconheceu os Bañados del Este, um sítio Ramsar e suas zonas úmidas como parte da Reserva da Biosfera da Unesco (Probides, 1999). Em território brasileiro, a Estação Ecológica do Taim faz parte da rede de Reservas da Mata Atlântica, do Programa Man and the Biosphere (MAB) da Unesco, além das reservas biológicas estaduais como a do Mato Grande, Maçarico e Bioma Pampa. As terras que ficam ao entorno da Lagoa Mirim e do Canal São Gonçalo são dedicadas à agricultura. Antes de 1977, as condições da água da Lagoa apresentavam-se salobra devido a ligação do estuário da Lagoa dos Patos que desaguava na Lagoa Mirim. Após esse período, a Lagoa torna-se um reservatório de água doce semiaquático devido à construção da barragem do canal São Gonçalo para romper a entrada de água salina do estuário da Lagoa dos Patos na Lagoa Mirim para que assim começasse a irrigação da plantação de arroz (Bueno et al., 2021). Com isso, a principal utilização das águas da Lagoa Mirim envolve a extração direta para irrigação das plantações de arroz. Além disso, a lagoa serve como fonte de água potável para as populações que vivem em seu entorno (Oliveira et al., 2015). A Figura 4 mostra a localização da Bacia Hidrográfica da Lagoa Mirim, evidenciando seu caráter transfronteiriço entre o Brasil e o Uruguai. O mapa apresenta o limite da bacia, a Lagoa Mirim e a distribuição territorial entre os dois países.

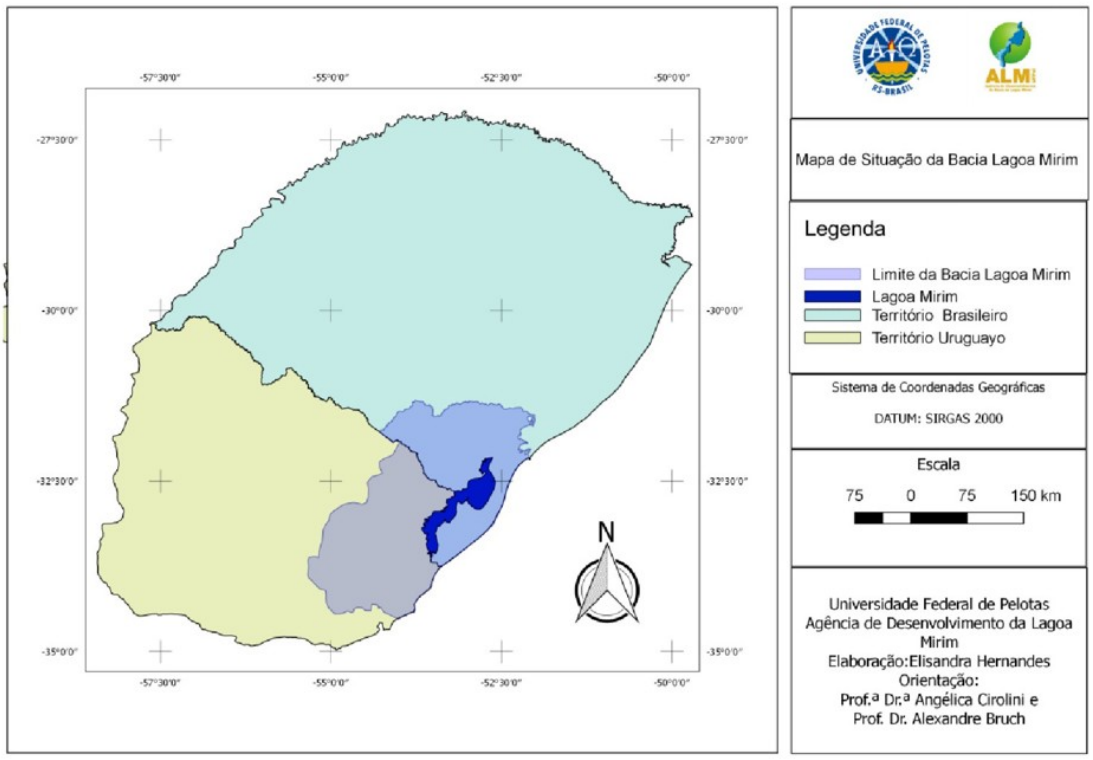


Figura 4. Mapa de localização da Bacia Hidrográfica da Lagoa Mirim. Fonte: Agência de Desenvolvimento da Lagoa Mirim (ALM), 2022.

A Agência de Desenvolvimento da Lagoa Mirim (ALM), criada em 1994 vinculada a Universidade Federal de Pelotas (UFPEL), possui a responsabilidade de avaliar a qualidade da água da bacia mensalmente em diferentes pontos ao longo da lagoa, desde o Canal São Gonçalo até Santa Vitória do Palmar. Nessas avaliações são considerados os parâmetros físico-químicos e microbiológicos da água. Ao longo dos anos foram desenvolvidos estudos no local abordando aspectos da qualidade da água, no entanto demonstram escassez de trabalhos e a falta de um monitoramento de longo prazo, principalmente sobre a ocorrência de poluentes emergentes e agrotóxicos na Lagoa Mirim.

Como evidenciado acima, as características da região favorecem o desenvolvimento da agropecuária, tendo a criação de gado, produção de arroz e soja como suas principais atividades. Além do lançamento de efluentes domésticos e industriais na água. Consequentemente, agrotóxicos, antibióticos, hormônios e outros contaminantes emergentes podem potencialmente impactar os ecossistemas aquáticos da região, sua biota e a saúde humana que dependem desse recurso como fonte de água potável. Com relação ao agrotóxico- alvo do presente estudo, o imidacloprido foi encontrado em amostras de águas superficiais do Distrito de Irrigação do Chasqueiro (uma das Sub-Bacias da Bacia Hidrográfica Mirim - São Gonçalo), em um monitoramento anterior, no período que compreende o ciclo de irrigação do cultivo de arroz e consequentemente, a aplicação de agroquímicos na Lagoa Mirim (Corrêa et al., 2023).

Apesar do aumento no número de estudos sobre contaminantes emergentes em ambientes aquáticos continentais no Brasil, ainda existem lacunas importantes relacionadas à ocorrência desses compostos em bacias hidrográficas, especialmente na Lagoa Mirim. Além disso, são escassas as avaliações integrando dados de monitoramento ambiental com testes ecotoxicológicos comparativos utilizando espécies tropicais e temperadas, o que limita a compreensão dos riscos ecológicos associados à presença desses contaminantes na região.

Dessa forma, avaliar a ocorrência dos contaminantes emergentes nessa bacia hidrográfica é vital pra dimensionar os impactos tanto no ecossistema, quanto na saúde humana. Nesse sentido, foram realizadas coletas de água com o intuito de avaliar a ocorrência de vinte e seis contaminantes emergentes em pontos estratégicos na bacia hidrográfica da Lagoa Mirim. A seleção dos contaminantes buscou abranger substâncias de interesse ambiental pertencentes a diferentes classes químicas e associadas a potenciais fontes antrópicas presentes na bacia da Lagoa Mirim, especialmente atividades agrícolas e aportes urbanos. Ainda, os locais de amostragem foram selecionados para representar áreas com maior influência rural e agrícola; áreas localizadas ao longo das margens da Lagoa Mirim com ocupação local e usos recreativos; e uma área de uso múltiplo associada a uma área portuária – Porto Santa Vitória – e a influência urbano-rural do município de Santa Vitória do Palmar. O estudo também considerou a variação temporal associada ao ciclo do arroz irrigado, com amostragem realizada em quatro períodos: T1 e T2, correspondentes ao período de irrigação dos arrozais; T3, associado à drenagem da água utilizada nos campos antes da colheita; e T4, correspondente à entressafra, período de menor atividade agrícola.

Juntamente com as coletas das amostras de água, foi realizada uma revisão sistemática da literatura científica sobre contaminantes emergentes, qualidade da água e metais pesados na região entre os anos 2001 e 2025. A integração dessas informações com dados das coletas de água em quatro períodos associados ao ciclo do arroz irrigado (T1–T4) e os dados da literatura da região da Lagoa Mirim, contribuiu para o estabelecimento de uma base de referência atualizada e para o fortalecimento do conhecimento sobre a qualidade ambiental desse importante sistema aquático.

Além disso, em laboratório, foram avaliados e comparados os potenciais efeitos do agrotóxico imidacloprido, em quatro organismos-teste aquáticos pertencentes ao zooplâncton, sendo *Daphnia similis, D. magna, Ceriodaphnia dubia* (espécies exóticas) e *C. silvestri* (espécie nativa).

Assim, as hipóteses do primeiro capítulo foram que: (i) contaminantes ambientais, particularmente herbicidas, inseticidas, fungicidas e metabólitos de compostos associados a atividades agrícolas (cultivo de arroz), juntamente com cafeína e compostos associados a esgoto doméstico e assentamentos urbanos estão presentes nas águas superficiais da bacia hidrográfica da Lagoa Mirim, refletindo a influência combinada dos usos do solo agrícola e urbano; (ii) parâmetros físico-químicos e microbiológicos, particularmente fósforo total e coliformes termotolerantes, excedem os limites estabelecidos pela Resolução CONAMA nº 357/2005

para águas doces de Classe 2 em locais específicos da bacia da Lagoa Mirim, em consonância com estudos anteriores realizados na região (Fia et al., 2009; Corrêa et al., 2022; Drose et al., 2020; Pinto et al., 2020; Valentini et al., 2021; Silva et al., 2024), refletindo o enriquecimento persistente por nutrientes decorrente do escoamento de fertilizantes agrícolas e da pecuária, bem como a contaminação fecal associada à falta de infraestrutura de tratamento de esgoto doméstico nos municípios do entorno; (iii) as concentrações de contaminantes ambientais variam ao longo do tempo em associação com o ciclo do arroz irrigado (T1–T4) e as condições hidroclimáticas da bacia, tais como variabilidade da precipitação, períodos secos e chuvosos e flutuações sazonais de temperatura típicas do clima subtropical úmido da região (Alvares et al., 2013; Marengo et al., 2024) — esperando-se maiores cargas de contaminantes durante os períodos de irrigação/drenagem (T1–T3) e em condições de baixa pluviosidade que reduzem a capacidade de diluição da lagoa; e (iv) a literatura científica disponível sobre a ocorrência de contaminantes ambientais (agrotóxicos, fármacos e outros contaminantes emergentes) permanece escassa e concentra-se predominantemente em parâmetros convencionais de qualidade da água na bacia da Lagoa Mirim.

As hipóteses do segundo capítulo foram que: (i) o cladócero nativo de porte relativamente pequeno *C. silvestri*i seria mais sensível à exposição aguda ao imidacloprido do que *D. magna*, *D. similis* e *C. dubia*, apresentando uma CE_{50} de imobilização em 48 h mais baixa; (ii) diferenças interespecíficas no comportamento alimentar, na taxa de filtração e nas respostas fisiológicas resultariam em uma maior inibição da ingestão de algas por *C. silvestrii*; e (iii) a exposição prolongada ao imidacloprido comprometeria a alocação de energia para a reprodução, reduzindo a produção de neonatos por *D. magna* e *D. similis* em relação aos seus respectivos grupos-controle.

OBJETIVOS

Objetivo Geral

Analisar a ocorrência de contaminantes ambientais em águas superficiais na bacia hidrográfica da Lagoa Mirim, Sul do Brasil, e avaliar os efeitos do inseticida imidacloprido em espécies de zooplâncton pertencentes a diferentes gêneros.

Objetivos específicos

(1) Realizar uma revisão sistemática da literatura científica sobre a ocorrência de contaminantes emergentes, agrotóxicos, metais pesados, microplásticos, fármacos e indicadores de qualidade da água na bacia hidrográfica da Lagoa Mirim;

(2) Verificar a ocorrência e quantificar as concentrações de vinte e seis contaminantes em pontos estratégicos na bacia hidrográfica da Lagoa Mirim;

(3) Integrar os dados obtidos na literatura com resultados de monitoramento ambiental realizados em quatro tempos amostrais (T1–T4);

(4) Avaliar e comparar os efeitos letais e subletais da exposição ao imidacloprido em *Ceriodaphnia silvestrii* (espécie nativa), *C. dubia*, *Daphnia magna* e *D. similis* (espécies exóticas), considerando os parâmetros sobrevivência, taxa de filtração alimentar e reprodução.

(5) Comparar a sensibilidade das espécies *D. magna*, *D. similis*, *C. silvestrii* e *C. dubia* ao imidacloprido por meio da construção de curvas de distribuição de sensibilidade das espécies (SSD), seguida por uma avaliação de risco ecológico.

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CAPÍTULO 1

Environmental contaminants in a strategic transboundary river basin: an assessment of occurrence in Mirim Lagoon (southern Brazil)

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Abstract

The Lagoa Mirim watershed, located in southern Brazil and Uruguay, is a strategic transboundary system affected by agricultural and urban pressures. This study evaluated environmental contaminants and water quality in the Brazilian portion of Lagoa Mirim and integrated the results with a systematic review of studies published between 2001 and 2025. Surface water samples were collected at six sites during the irrigation (T1 and T2), pre-harvest drainage (T3), and rice off-season (T4) periods. Physicochemical and microbiological parameters were assessed, and 26 compounds were analyzed using liquid chromatography-mass spectrometry. Twenty-two compounds were detected, including pesticides, triazine metabolites, caffeine, and trimethoprim. Tebuconazole showed the highest concentration (4,999 ng L^{-1}), followed by 2,4-D (628 ng L^{-1}), caffeine (618 ng L^{-1}), imidacloprid (181 ng L^{-1}), and thiamethoxam (179 ng L^{-1}). Tebuconazole and azoxystrobin were detected in all samples, while atrazine, metolachlor, caffeine, and the triazine metabolite 2-hydroxyatrazine showed detection frequencies of 95.8%. Contaminants were present during all periods, including the off-season, without a clearly defined temporal or spatial pattern, indicating continuous inputs, multiple sources, environmental persistence, and dispersion within the lagoon. Total phosphorus reached 0.12 mg L^{-1}, while thermotolerant coliforms reached 92,000 MPN 100 mL^{-1}, exceeding Brazilian regulatory limits at specific sites. The systematic review included 19 studies, predominantly addressing conventional water quality parameters and metals, with only two focusing on pesticides and one on emerging contaminants. This first integrated assessment provides an updated baseline for contaminant monitoring and transboundary water management in the Lagoa Mirim region.

Keywords: Antibiotic; Caffeine; Irrigated rice; Pesticides; Water quality.

Introduction

Human activities have contributed to the release of chemical compounds into water bodies (Li et al., 2025). With advances in analytical capacity and improvements in detection techniques, it has become possible to analyze compounds that were previously not detected in these ecosystems (Richardson & Ternes, 2022). In this context, contaminants of emerging concern (CECs) have gained attention, a term used to refer to substances released into the environment for which there is still no specific regulation or widely established legal limits (Tang et al., 2019). Examples of emerging contaminants include beauty and personal care products, pharmaceuticals, hormones, pesticides, microplastics, solvents, flame retardants, some metals, and industrial compounds, such as polychlorinated biphenyls, bisphenol, phthalates, and organotins, among others (Reichert et al., 2019; UNESCO, 2021).

Concern about these contaminants arises from the widespread use of these substances in daily activities by a large portion of the population. As a result, they have been frequently detected in water, sediments, soils, the atmosphere, plants, living organisms, food products, protected species, and even in areas with no apparent anthropogenic activity, highlighting their broad environmental dispersion on a global scale (Deblonde et al., 2011; Galindo-Miranda et al., 2019; Routti et al., 2019). Emerging contaminants may originate from both point and non-point sources and can bioaccumulate through food webs, negatively affecting wildlife and human health (Tang et al., 2019). This situation mainly results from the discharge of urban, hospital, industrial, and agricultural effluents, combined with the limitations of conventional processes used in wastewater treatment plants, which are not effective to remove these compounds (Morin-Crini et al., 2022). The occurrence, monitoring, and assessment of contaminants in Brazilian water bodies are still limited (Montagner et al., 2017; Petrie et al., 2015; Quadra et al., 2017; Ribas et al., 2021).

Among pharmaceuticals, antibiotics represent an important environmental concern, as they can affect non-target aquatic organisms and favor processes related to bacterial resistance (Li et al., 2025). Some Asian countries, as well as countries in North America and Europe, exhibit high detection frequencies of antibiotics due to high population density, well-developed healthcare infrastructure, and substantial consumption of these medications (Zhang et al., 2024). Intensive livestock farming and aquaculture activities may further amplify the discharge of antibiotics into the environment (Haenni et al., 2022). Still within the context of urbanization, caffeine has also gained attention and has been frequently detected in aquatic environments due to its widespread use, representing a considerable threat to aquatic ecosystems (Anastopoulos et al., 2020). Caffeine has been used as a chemical marker of domestic wastewater contamination because of its association with human consumption and sewage discharge into aquatic environments (Montagner et al., 2014; Gonçalves et al., 2017).

Among the various substances affecting aquatic environments, pesticides are considered one of the main threats to the conservation of continental aquatic biodiversity worldwide (Sánchez-Bayo & Hyne, 2011). These chemicals have been increasingly used to enhance agricultural production and crop quality by minimizing damage to cultivated plants (Riascos-Flores et al., 2021). In 2024, approximately 825,793 tons of pesticide active ingredients were sold in Brazil, of which 88,913 metric tons (10.8%) were commercialized in the state of Rio Grande do Sul (IBAMA, 2025). However, due to the high usage of these products, pesticides are transported to and detected in inland aquatic ecosystems via surface runoff, transport, leaching, and infiltration (Acayaba et al., 2021). Irrigated rice cultivation, for example, is an activity with considerable environmental impact due to the potential transport of pesticides to natural aquatic environments (Scorza Junior et al., 2017).

This context is particularly relevant in southern Brazil, where irrigated rice cultivation is a major agricultural activity in Rio Grande do Sul, especially in floodplain and coastal plain areas. The state is Brazil's largest rice producer, and the Lagoa Mirim watershed region (in southern Brazil) is closely linked to this agricultural activity (Pinto et al., 2020; IRGA, 2024; CONAB,

2025). The Lagoa Mirim watershed, located on the border between the state of Rio Grande do Sul (in southernmost Brazil) and Uruguay, is one of the region's major watersheds; together with the Lagoa dos Patos, it forms the largest lagoon complex in South America (Silva et al., 2024). Covering a total area of 62,250 km², this watershed is a significant system in South America, playing crucial ecological and economic roles related to agriculture in both Rio Grande do Sul and Uruguay (Oliveira et al., 2015). As previously reported, the region's characteristics, such as abundant water resources, wetlands, and plains suitable for irrigation, favor the development of agricultural and livestock activities, with cattle ranching and rice cultivation being among the primary ones. Furthermore, integrated crop-livestock systems and crop rotations involving rice, soybeans, and pastures are common in the area (Sosinski, 2009; FEPAM, 2021). Consequently, pesticides, antibiotics, and other emerging contaminants may affect the region's aquatic ecosystems, their biota, and the health of human populations relying on this resource for drinking water. This knowledge gap hinders the understanding of potential ecological and human health risks within this transboundary watershed in southern South America, given that these substances can cross borders and impact regions far beyond their point of origin.

In this context, the present study aimed to evaluate the occurrence of environmental contaminants at strategic points within the Lagoa Mirim watershed, covering varying land-use and land-cover conditions. Sampling sites were selected to represent areas with significant rural and agricultural influence; areas situated along the shores of Mirim Lagoon, characterized by local settlement and recreational use; and a multi-use area associated with a port zone and the urban-rural influence of the municipality of Santa Vitória do Palmar. Furthermore, a systematic review of the scientific literature was conducted to assess the history of environmental contaminant occurrence and water quality in the region between 2001 and 2025.

The hypotheses of this study were that: (i) environmental contaminants—particularly herbicides, insecticides, fungicides, and metabolites of compounds associated with agricultural activities (rice cultivation), along with caffeine and compounds associated with domestic sewage and urban settlement—are present in the surface waters of the Lagoa Mirim watershed, reflecting the combined influence of agricultural and urban land uses; (ii) physicochemical and microbiological parameters, particularly total phosphorus and thermotolerant coliforms, exceed the limits established by CONAMA Resolution No. 357/2005 for Class 2 freshwaters at specific locations within the Lagoa Mirim watershed, consistent with previous studies conducted in the region (Fia et al., 2009; Corrêa et al., 2022; Drose et al., 2020; Pinto et al., 2020; Valentini et al., 2021; Silva et al., 2024), reflecting persistent nutrient enrichment resulting from agricultural fertilizer runoff and livestock farming, as well as fecal contamination associated with the lack of domestic sewage treatment infrastructure in surrounding municipalities; (iii) concentrations of environmental contaminants vary over time in association with the irrigated rice cycle (T1–T4) and the watershed's hydroclimatic conditions—such as precipitation variability, dry and wet periods, and seasonal temperature fluctuations typical of the region's humid subtropical climate (Alvares et al., 2013; Marengo et al., 2024)—with higher contaminant loads expected during irrigation/drainage periods (T1–T3) and under low-rainfall conditions that reduce the lagoon's dilution capacity; and (iv) The available scientific literature on the occurrence of environmental contaminants (pesticides, pharmaceuticals, and other CECs) remains scarce and focuses predominantly on conventional water quality parameters in the Lagoa Mirim watershed.

To the best of our knowledge, this study presents the first integrated assessment combining the determination of pesticides, herbicide metabolites, caffeine, and antibiotics with physicochemical and microbiological analyses of surface waters from Lagoa Mirim, alongside a systematic review of studies published between 2001 and 2025 regarding emerging contaminants, metals, and water quality in the region. These updated results can contribute to future monitoring programs, environmental risk assessments, and integrated water quality management in this important transboundary aquatic system.

Materials and methods

Systematic review

A systematic literature review was conducted to identify peer-reviewed studies addressing water quality and environmental contaminants in the Mirim Lagoon watershed. Searches were performed in Google Scholar, SciELO, and Web of Science. The first search was conducted in February 2026, and the final search update was performed on July 1, 2026. The review included studies published between January 2001 and December 2025 (Table S1), as this was the time interval represented by the articles retrieved from the consulted databases that met the thematic and geographic criteria of the review.

The search strategy included combinations of the following keywords: “Lagoa Mirim”, “Mirim Lagoon”, and “Bacia Hidrográfica da Lagoa Mirim”. These terms were combined with keywords related to water quality and contaminants, including “water quality”, “qualidade da água”, “contaminants”, “contaminantes”, “pollutants”, “pesticides”, “agrotóxicos”, “heavy metals”, “metais pesados”, “emerging contaminants”, “contaminantes emergentes”, and “microplastics”, using Boolean operators (AND, OR).

The selection process was conducted in two sequential stages. First, titles and abstracts were screened to exclude records that were not related to the scope of the review. Next, the full texts of potentially eligible articles were assessed according to previously defined inclusion and exclusion criteria. Studies were included when they met all of the following criteria: (i) peer-reviewed scientific article; (ii) conducted in the Mirim Lagoon watershed; and (iii) addressed water quality and/or environmental contaminants, including physicochemical and microbiological parameters, heavy metals, pesticides, pharmaceuticals, caffeine, plastics, or other emerging contaminants.

Studies were excluded when they were outside the study area, were not peer-reviewed, were duplicates, or were not related to water quality or environmental contamination. A decision matrix was applied to standardize the eligibility assessment and reduce subjectivity during article selection (Table S2). Each record was evaluated according to predefined inclusion and exclusion codes, and the final decision was recorded as included or excluded. The final set of included studies was characterized according to year of publication, study area, environmental matrix, objective, methodological approach, and parameters evaluated. The studies were grouped into four main categories: water quality, heavy metals, pesticides and agricultural pressure, and emerging contaminants. Studies retrieved from more than one database were counted only once.

Study area and sampling sites

The study area comprises the Mirim Lagoon watershed, located in the southernmost region of the state of Rio Grande do Sul, between the geographic coordinates 31°30′ and 34°35′ S and 53°31′ and 55°15′ W, covering an area of approximately 62,250 km², of which about 47% lies in Brazilian territory and 53% in Uruguayan territory (Coradi et al., 2009). This watershed represents an important system in South America, playing both ecological and economic roles related to agriculture in the state of Rio Grande do Sul and Uruguay (Oliveira et al., 2015). The regional climate is classified as humid subtropical with hot summers, characterized by mean temperatures above 22 °C in the warmest months and below 18 °C in the coldest months, with an average annual rainfall of 1,450 mm (Alvares et al., 2013; Cardoso et al., 2024).

The biodiversity of the watershed is extremely important for the conservation of landscapes and ecosystems, including the Atlantic coastal zone with lakes and lagoons in both countries; several low-lying wetland areas associated with lagoons and forests with rich biodiversity; the Pampa biome and riparian and wet forests; and upland areas associated with the Serra do Sudeste system (Cordeiro & Hasenack, 2009). Wetlands play a fundamental role due to the richness of fauna and flora they

support, in addition to serving as refuges for migratory birds. They also perform essential functions in regulating river flow, controlling floods, recharging aquifers, and improving water quality. Furthermore, they have great sociocultural relevance and are valued for their scenic and landscape beauty (MMA, 2000).

In Uruguayan territory, the government recognized Bañados del Este, a Ramsar site, and its wetlands as part of the UNESCO Biosphere Reserve (PROBIDES, 1999). In Brazilian territory, the Taim Ecological Station is part of the Atlantic Forest Reserves network under UNESCO's Man and the Biosphere (MAB) Programme, in addition to state biological reserves such as Mato Grande, Maçarico, and Bioma Pampa. The lands surrounding Mirim Lagoon and the São Gonçalo Channel are mainly dedicated to agriculture. The main use of Mirim Lagoon waters involves direct withdrawal for irrigation of rice fields. In addition, the lagoon serves as a source of drinking water for the populations living in its surroundings (Oliveira et al., 2015).

Surface water samples were collected at six sites along Mirim Lagoon (see Fig 1 and Table S1 in the Supplementary Material), all of which are routinely monitored by the Agência de Desenvolvimento da Lagoa Mirim (ALM). The sampling sites were selected based on ALM's monitoring history, their spatial distribution along the lagoon, and the study by Corrêa et al. (2022), which reported the occurrence of pesticides in surface waters from adjacent areas connected to the lagoon. This sampling design also aimed to provide an updated characterization of the lagoon's water conditions regarding the presence of emerging contaminants.

The six sampling points were distributed along the western and eastern shores of Mirim Lagoon, covering areas with varying degrees of agricultural and urban influence. Point P1 is located at the Arroio Grande River, P2 at Pontal Beach, P3 at São Francisco Farm, P4 at Capilha, P5 at Vila Anselmi, and P6 at Porto Santa Vitória. The geographic coordinates for the six points are provided in Table S3 of the supplementary material. Sampling was organized into four time points (T1–T4), defined according to different stages of the irrigated rice cycle in the Lagoa Mirim region: T1 and T2 (January and February), associated with active crop development under irrigation; T3 (March), associated with crop maturation and field drainage prior to harvest; and T4 (July), corresponding to the off-season, when the rice fields are outside the active growing period (CONAB, 2022; IRGA, 2024, 2026; Scivittaro et al., 2021).

To this end, two 500 mL surface water samples were collected at each sampling point (P1 through P6), totaling 1 L per point. Samples were collected at a depth of approximately 20 cm using a stainless-steel bucket, transferred into new, previously unused polypropylene containers, and immediately kept on ice during transport. Upon arrival at the laboratory, the samples were stored at −20 °C until quantitative analysis (ABNT NBR 15469, 2016).

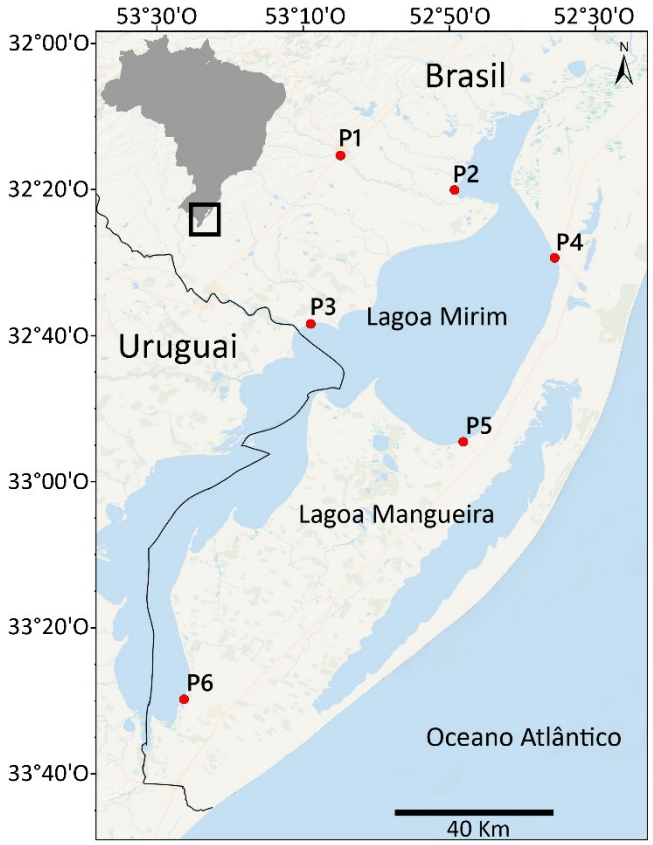


Fig. 1 The study area comprises the five sampling points (P2, P3, P4, P5 and P6) along the Mirim Lagoon and one (P1) in a tributary.

Physicochemical and thermotolerant coliforms of the sampling sites

The physical and chemical variables analyzed in the collected samples were: pH, temperature, conductivity, salinity, total phosphorus, total nitrogen, thermotolerant coliforms, organic matter, biochemical oxygen demand, dissolved oxygen, turbidity, total solids, and chlorophyll-a. Parameters such as pH, temperature, and conductivity were measured directly in the field using a K39-003PHC multiparameter probe (Kasvi). Parameter concentrations were quantified using methodologies according to the official method for water analysis (APHA, AWWA; WEF, 2012) by professionals from the Agência de Desenvolvimento da Lagoa Mirim (ALM). Subsequently, the values were compared with the limits established by Resolution No. 357 of the National Environmental Council (CONAMA) for Class 2 waters, into which the study area is classified (Table S4 in the Supplementary Material). CONAMA Resolution No. 357/2005 provides for the classification of surface water bodies and establishes guidelines for their classification, in addition to defining water quality conditions and standards and effluent discharge standards in Brazil.

Chemical analysis of water at the sampling sites

After collection, water samples were kept frozen and protected from light until laboratory processing. Solid-phase extraction was performed using 500 mg OASIS HLB cartridges (Waters, Milford, USA). Prior to sample application, the

cartridges were conditioned with methanol and water. After the samples had passed through, the retained analytes were eluted with methanol and acetonitrile, using 4 mL of each solvent. The resulting extract was dried under a stream of N_2 (LabTech MultiVap 54, Sorisole, Italy). Subsequently, the samples were reconstituted in 500 µL of a methanol: water solution (30:70, v/v) containing internal standards at a concentration of 50 µg L^{-1}. The final extracts were filtered using polytetrafluoroethylene syringe filters (13 mm, 0.22 µm; Analítica, Brazil). The samples were analyzed by liquid chromatography coupled with tandem mass spectrometry (LC–MS/MS) (Thermo Vanquish–TSQ Fortis, Massachusetts, USA) in both positive and negative ionization modes. Analytical curves were prepared at concentrations ranging from 0.5 to 500 µg L^{-1}. Limits of quantification (LOQ) and detection (LOD) were determined based on the signal-to-noise ratio, using ratios of 10:1 and 3:1, respectively. The detection frequency and the minimum, maximum, and mean concentrations of emerging contaminants in the water samples from Lagoa Mirim are presented in Fig. S3 of the Supplementary Material.

Data analysis

Linear discriminant analysis (LDA) of physicochemical data

Total solids and salinity were excluded from the analysis because they showed high collinearity with turbidity and electrical conductivity. Highly correlated variables ($r > 0.7$) were identified through correlation analysis and removed in order to reduce collinearity and avoid redundancy in the data matrix. Subsequently, the data were standardized using z-scores to ensure comparability among variables measured on different scales. Linear discriminant analysis (LDA) was used to assess differentiation among sampling periods, considering period as the categorical variable (grouping factor) and the physicochemical variables as predictors. The relative importance of the variables in discriminating among groups was evaluated based on the coefficients of the discriminant axes, with emphasis on the first axis (LD1), which represented the main environmental gradient. The predictive performance of the model was assessed using leave-one-out cross-validation (LOOCV), with overall accuracy and the Kappa coefficient calculated to quantify model performance relative to chance. Additionally, a confusion matrix was generated to evaluate the classification pattern among groups. The analyses were conducted in the R environment using the MASS package.

Multivariate analyses of emerging contaminants

Variation in the composition of emerging contaminants in water samples was assessed using multivariate analyses. First, Principal Component Analysis (PCA) was performed to explore patterns in contaminant distribution and to identify possible spatial and temporal trends in the data. For inferential statistical analysis, permutational multivariate analysis of variance (PERMANOVA) was applied to test for differences in contaminant composition among sampling periods. Values below the LOQ were replaced by half of the limit of quantification value (LOQ/2). The data were then log-transformed using base 10 [$\log_{10}(x + 1)$] to reduce asymmetry and minimize the influence of extreme values. Similarity among samples was calculated using Bray–Curtis distance. PERMANOVA was applied to test for differences in contaminant composition among sampling periods using 999 permutations. Considering the sampling design with repeated measurements at the same sites over time, the spatial structure was incorporated as a restriction factor in the permutations, when applicable. The homogeneity of multivariate dispersion among groups was evaluated using the dispersion test (betadisper) to determine whether any differences detected by PERMANOVA were associated with variation in within-group dispersion. All analyses were performed in the R environment (RStudio), using the vegan and stats packages.

Results and discussion

Systematic review

The database search identified 34 studies: 19 from Google Scholar, 1 from SciELO, and 14 from Web of Science. After removing duplicates and applying the eligibility criteria, 19 studies were included in the qualitative synthesis (Fig. S1). Water-quality studies predominated (11 studies; 57.9%), followed by heavy-metal studies (5; 26.3%), pesticides and agricultural pressure (2; 10.5%), and emerging contaminants (1; 5.3%). The main characteristics and findings of these studies are summarized in Table 1, whereas detailed information on sampling design, analytical methods and quantitative results is provided in Table S1.

Table 1. Summary of studies included in the qualitative synthesis of environmental quality in Mirim Lagoon and its hydrologically connected tributaries (n = 19).

Thematic category	Studies, n (%)	Matrices and approaches	Main synthesis	References
Water quality	11 (57.9%)	Surface water; field/laboratory monitoring, WQIs, multivariate statistics, biomarkers and remote sensing.	Total phosphorus, turbidity/solids, dissolved oxygen and thermotolerant coliforms were recurrent drivers. Satellite studies supported spatial monitoring of chlorophyll-a and turbidity.	Fia et al. (2009); Pinto et al. (2020); Drose et al. (2020); Valentini et al. (2020, 2021a, 2021b); da Silveira et al. (2021); Caballero et al. (2022); Caballero (2023); Borges et al. (2023); Silva et al. (2024)
Heavy metals	5 (26.3%)	Fish muscle, surface sediments, sediment cores, and dissolved/particulate water fractions.	Concentrations were generally low or close to regional background. No broad enrichment was found in surface sediments, although recent Ba enrichment in cores was associated with coal mining/combustion.	Niencheski et al. (2001); Santos et al. (2003); Mirlean et al. (2003); Friedrich et al. (2006); Bueno et al. (2025)
Pesticides and agricultural pressure	2 (10.5%)	Palaeolimnology in Mirim Lagoon and pesticide monitoring in three hydrologically connected tributaries.	Agricultural intensification and water-locking were associated with increased sedimentation. In tributaries, 24 pesticides were detected; azoxystrobin and tricyclazole were the most frequent (78%).	Bueno et al. (2021); Corrêa et al. (2022)

Thematic category	Studies, n (%)	Matrices and approaches	Main synthesis	References
Emerging contaminants	1 (5.3%)	Dated sediment cores and microplastic characterization.	Microplastics occurred in dated sediments; rayon, PVC and acrylate were among the most common polymers.	Alves et al. (2023)

Physicochemical and thermotolerant coliform parameters of the sampling sites

The results of the physicochemical and thermotolerant coliform analyses of the water, carried out at different sampling points throughout the four sampling periods (T1–T4), defined according to the different phases of the agricultural cycle in the Lagoa Mirim region, are presented in Table S4 of the Supplementary Material. The physicochemical and thermotolerant coliform parameters showed spatial and temporal variations throughout the monitoring period in Lagoa Mirim. In general, pH, temperature, turbidity, total solids, and dissolved oxygen remained within the limits established by CONAMA Resolution No. 357/2005 for Class 2 waters. However, thermotolerant coliforms exceeded the limit of 1000 MPN/100 mL at some points, especially at point P1, which recorded the highest values in T1, T2, and T3 (35,000, 92,000, and 1,100 MPN/100 mL, respectively). Point P4 also showed a high value at T2 (1,600 MPN/100 mL).

Total phosphorus was detected only during T4, with concentrations ranging from 0.03 to 0.12 mg/L; the highest values were observed at point P5 during T4 (0.12 mg/L) and at P1 (0.08 mg P L), exceeding the regulatory limit (0.03 mg/L), while P2, P3, and P6 showed 0.04 mg P L, values slightly above the limit. Point P4 showed 0.03 mg P L, remaining at the maximum permitted value. Salinity showed higher values at site P5 in T3 and T4, indicating a possible influence of dissolved salts in the region. The results of the Linear Discriminant Analysis (LDA) of the physicochemical and thermotolerant coliforms in the water during the different sampling periods in the Mirim Lagoon are presented in Fig 2.

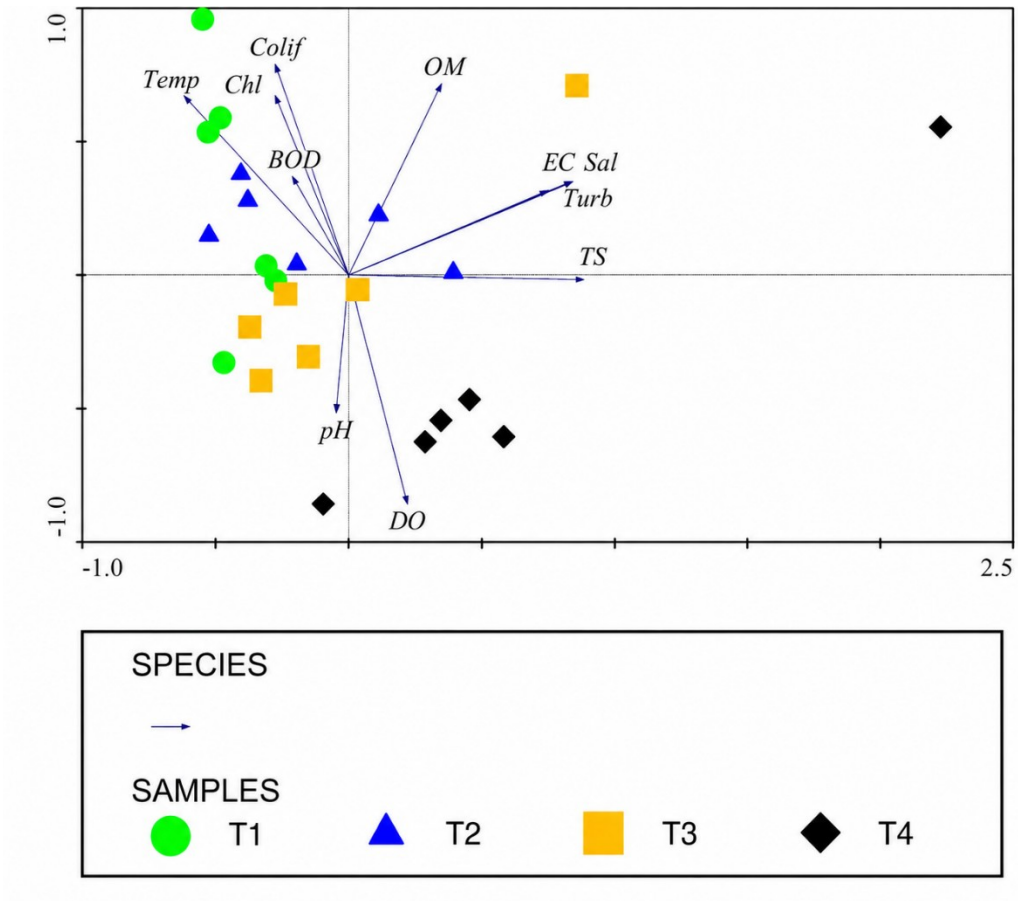


Fig. 2 Linear discriminant analysis (LDA) of physicochemical variables in water samples from Lagoa Mirim, collected during the four sampling periods (T1-T4). T1 and T2 correspond to the irrigation period of the rice fields, T3 represents the water drainage period before harvest, and T4 corresponds to the off-season. The points represent the samples per period, and the arrows indicate the environmental variables. The separation of the groups along the discriminant axis reflects differences in physicochemical conditions between the sampling periods

Linear Discriminant Analysis (LDA) showed that the first discriminant axis (LD1) explained 98% of the data variance, whereas the second axis had low discriminatory capacity (1.7%). The variables that contributed most to data structuring were dissolved oxygen (DO) (3.69), followed by temperature (2.30), turbidity (2.03), and biochemical oxygen demand (BOD) (1.01). Other variables, such as pH (0.66), organic matter (OM) (0.54), coliforms (0.29), and electrical conductivity (EC) (0.21), showed lower explanatory power. The ordination revealed a clearer separation of samples collected in T4 from the other periods, whereas T1, T2, and T3 showed substantial overlap, suggesting greater environmental similarity among these periods. Cross-validation of the model showed an overall accuracy of 60.9% and a Kappa coefficient of 0.48, indicating moderate discriminant capacity, although significantly higher than expected by chance ($p < 0.001$).

The complete set of physicochemical and thermotolerant coliforms parameters is presented in Table S4 of the Supplementary Material. In the main text, only the parameters that were not in compliance with the limits established by CONAMA Resolution No. 357/2005 are highlighted. Among the parameters analyzed, total phosphorus and thermotolerant coliforms were above the limits established for Class 2 freshwater. Total phosphorus exceeded the limit established for lentic environments, of 0.030 mg L^{-1}, with values ranging from 0.03 to 0.12 mg L^{-1}. Thermotolerant coliforms also exceeded the limit of 1.000 MPN 100 mL^{-1}, reaching 35.000 MPN 100 mL^{-1} at T1 at point P1, 1.600 MPN 100 mL^{-1} at T2 at point P4, and 92,000 MPN 100 mL^{-1} at T3 at point P1. These results are consistent with previous studies carried out in Lagoa Mirim. Silva et al. (2024) recorded high concentrations of thermotolerant coliforms at point P1 during all monitoring periods, with values of 7.900, 13.000 and 4.900 MPN 100 mL^{-1} in T1, T3 and T4, respectively, while point P4 showed a high value only in T1, reaching 4.900 MPN 100 mL^{-1}.

The high values of thermotolerant coliforms observed at some sites in Mirim Lagoon indicate possible fecal contamination, likely associated with domestic effluent discharge and runoff from surrounding livestock and animal husbandry areas. These microorganisms are important indicators for the characterization, identification, and classification of water quality (Ghildyal, 2018). Site P1 is located near the city of Arroio Grande, one of the localities that lacks a domestic wastewater treatment plant (Godecke & Decker, 2014). Furthermore, it represents the site with the highest percentage of urbanized area (5.34%) compared to the other sites, which could explain the thermotolerant coliform levels found in previous studies and in the present study. Regarding the high levels observed at P4, they may be related to increased recreational activity and the presence of bathers during the summer period, since this site corresponds to a beach area used for leisure. A study that evaluated the environmental quality of beaches based on bathing water quality showed that high concentrations of thermotolerant coliforms are frequently associated with domestic sewage discharge, increased tourist flow, and the input of contaminated stormwater runoff (Souza & Silva, 2015). Furthermore, it is the second-ranked location in terms of the percentage of urbanized area (0.41%).

In the same study, Silva et al. (2024) observed total phosphorus concentrations above the limit allowed by CONAMA Resolution No. 357/2005 (0.03 mg/L) in sampling periods T1 and T2. In the present study, although total phosphorus was quantified only in T4, concentrations ranged from 0.03 to 0.12 mg/L, with values above the legal limit at some sampling sites, indicating persistent nutrient inputs into Mirim Lagoon. Other studies conducted in the lagoon have reported the same pattern for these variables (Corrêa et al., 2022; Fia et al., 2009; Pinto et al., 2020; Drose et al., 2020; Valentini et al., 2021). In particular, nitrogen and phosphorus were found at elevated concentrations during the last six years of monitoring, between 2017 and 2022, at the studied sites (Table S5 in the supplementary material).This may be explained by the use of fertilizers in the surroundings of Mirim Lagoon, as runoff from croplands may carry phosphorus-rich fertilizers that ultimately contaminate the lagoon, especially at sites P2, P3, P4, P5, and P6, which are located close to agricultural zones (Drose et al., 2020; Valentini et al., 2021), or by livestock activities (Lap et al., 2021). These results were observed in a region where agricultural influence was noted in the surroundings of all sampling points, according to the land use and land cover analysis based on MapBiomas. The highest

percentages of agricultural areas were recorded at P1 (35.66%), P2 (29.70%), and P3 (24.01%), while P4, P5, and P6 showed 16.28%, 21.71%, and 14.43%, respectively.

T1 showed the highest chlorophyll-a values: P9 = 151 µg/L, P11 = 145.5 µg/L, and P12 = 150.5 µg/L. This also coincided with higher temperatures (~26–29 °C), suggesting a seasonal influence on phytoplankton productivity. This pattern is consistent with studies that associate higher chlorophyll-a concentrations with periods of higher temperature and greater nutrient availability, conditions that favor phytoplankton proliferation and may indicate eutrophication processes in aquatic environments (Guan et al., 2026). In the present study, the elevated chlorophyll-a values in T1, associated with higher temperatures, suggest a seasonal response of the system, possibly intensified by nutrient inputs during the period of greater agricultural activity. Alternatively, the positive correlation between total phosphorus and chlorophyll-a may favor phytoplankton productivity and indicate possible trophic enrichment of the aquatic system (Guimarães et al., 2023).

Multivariate analysis of physicochemical parameters and thermotolerant coliforms highlighted these seasonal differences across the sampling periods (Fig. 2). Samples from period T1 showed a stronger association with temperature, chlorophyll-a, thermotolerant coliforms, and biochemical oxygen demand. Samples from periods T2 and T3 showed a stronger association with turbidity, electrical conductivity, salinity, and total solids, whereas period T4 showed a stronger association with dissolved oxygen, likely due to lower temperatures and reduced biological activity. Pinto et al. (2020) demonstrated that water quality in Lagoa Mirim exhibits significant seasonal variation; the authors showed that temperature, dissolved oxygen, biochemical oxygen demand, total nitrogen, and total phosphorus were among the key parameters associated with seasonal differentiation. Corrêa et al. (2022) identified associations between parameters such as turbidity, total solids, and electrical conductivity and agricultural management periods in the same study area. According to the authors, the drainage of rice fields and surface runoff are directly linked to the limnological dynamics of the region's aquatic environments. Other authors working in rice-growing areas have also reported this relationship between water management in irrigated rice cultivation and changes in water quality. Studies conducted in rice fields in China and South Korea have demonstrated that artificial drainage, surface runoff, and precipitation events during the crop cycle influence the export of nutrients, solids, and diffuse pollutants, affecting parameters such as electrical conductivity, nitrogen loads, and the quality of water drained from the fields (Yu et al., 2021; Li et al., 2021; Wang et al., 2023; Jeon et al., 2025).

Analysis of emerging contaminants at the sampling sites

The identified compounds, as well as their respective concentrations across the sampling periods, are presented in fig 3. Table 2 presents the detection frequency, sampling periods, occurrence sites, compound classification, and the minimum, maximum, mean, and standard deviation concentrations of the analyzed contaminants.

Table 2. Frequency of detection, sampling points, chemical class, emergency status, and concentrations (minimum, maximum, average, and standard deviation) of contaminants in water samples from Lagoa Mirim. DIA, DEA, and 2HA correspond, respectively, to the triazine metabolites deisopropylatrazine, desethylatrazine, and 2-hydroxyatrazine.

Contaminant	Class	Emerging status	Detection frequency (%)	Detected times	Detected points	Concentration (ng L^{-1})			
						Min	Max	Mean	SD
2,4-D	Herbicide	Regulated (CONAMA 357/2005)	37.5	T1, T2, T3, T4	P1, P2, P3, P6	4	628	89	203
2HA	Triazine herbicide metabolite	Emerging / non-regulated	95.8	T1, T2, T3, T4	P1, P2, P3, P4, P5, P6	3	34	13	7

Contaminant	Class	Emerging status	Detection frequency (%)	Detected times	Detected points	Concentration (ng L^{-1})			
						Min	Max	Mean	SD
Ametryn (AMT)	Herbicide	Not detected	0.0	ND	ND	ND	ND	ND	ND
Atrazine (ATZ)	Herbicide	Regulated (CONAMA 357/2005)	95.8	T1, T2, T3, T4	P1, P2, P3, P4, P5, P6	4	24	10	4
Azoxistrobin (AZO)	Fungicide	Emerging / non-regulated	100.0	T1, T2, T3, T4	P1, P2, P3, P4, P5, P6	2	114	25	28
Caffeine (CAF)	Stimulant	Emerging / non-regulated	95.8	T1, T2, T3, T4	P1, P2, P3, P4, P5, P6	19	618	110	143
Carbendazim (CBZ)	Fungicide	Banned in Brazil	91.7	T1, T2, T3, T4	P1, P2, P3, P4, P5, P6	1	10	3	2
Carbofuran (CBF)	Insecticide	Banned in Brazil	33.3	T1, T2, T3	P1, P2, P3, P4, P6	1	9	3	3
Chlorpyrifos (CPF)	Insecticide	Not detected	0.0	ND	ND	ND	ND	ND	ND
DEA	Triazine herbicide metabolite	Emerging / non-regulated	95.8	T1, T2, T3, T4	P1, P2, P3, P4, P5, P6	5	20	12	5
DIA	Triazine herbicide metabolite	Emerging / non-regulated	87.5	T1, T2, T3, T4	P1, P2, P3, P4, P5, P6	2	13	8	3
Diuron (DIU)	Herbicide	Emerging / non-regulated	62.5	T1, T2, T3, T4	P1, P2, P3, P4, P5	3	21	8	6
Epoxiconazole (EPX)	Fungicide	Emerging / non-regulated	12.5	T1, T3	P2, P3	1	13	5	7
Fipronil (FIP)	Insecticide	Emerging / non-regulated	41.7	T1, T2, T3, T4	P1, P2, P3, P5	0	2	1	0
Hexazinone (HEX)	Herbicide	Not detected	0.0	ND	ND	ND	ND	ND	ND
Imidacloprid (IMI)	Insecticide	Emerging / non-regulated	91.7	T1, T2, T3, T4	P1, P2, P3, P4, P5, P6	1	181	15	37
Malathion (MAL)	Insecticide	Regulated (CONAMA 357/2005)	45.8	T1, T2, T3, T4	P1, P2, P3, P4, P5, P6	4	8	6	1
Metolachlor (MET)	Herbicide	Regulated (CONAMA 357/2005)	95.8	T1, T2, T3, T4	P1, P2, P3, P4, P5, P6	4	65	19	17
Profenofos (PFF)	Insecticide	Not detected	0.0	ND	ND	ND	ND	ND	ND
Propiconazole (PPZ)	Fungicide	Emerging / non-regulated	8.3	T2, T4	P4, P6	0	2	1	1
Simazine (SIM)	Herbicide	Regulated (CONAMA 357/2005)	45.8	T1, T2, T3, T4	P1, P2, P3, P5, P6	1	4	2	1
Tebuconazole (TEB)	Fungicide	Emerging / non-regulated	100.0	T1, T2, T3, T4	P1, P2, P3, P4, P5, P6	4	4999	473	1055
Tebuthiuron (TBT)	Herbicide	Emerging / non-regulated	79.2	T1, T2, T3, T4	P2, P3, P4, P5, P6	0	0	0	0
Thiamethoxam (TMX)	Insecticide	Emerging / non-regulated	83.3	T1, T2, T3, T4	P1, P2, P3, P4, P5, P6	2	179	23	40
Trifloxistrobin (TFS)	Fungicide	Emerging / non-regulated	4.2	T1	P6	2	2	2	0
Trimethoprim (TMP)	Antibiotic	Emerging / non-regulated	58.3	T1, T2, T3, T4	P1, P2, P3, P4, P5	0	2	1	1

Of the 26 compounds analyzed, 22 were detected, including eight herbicides, three triazine herbicide metabolites, seven insecticides, six fungicides, one stimulant, and one pharmaceutical/antibiotic, totaling 17 emerging contaminants. This is because five compounds detected in the samples of this study, atrazine, simazine, malathion, metolachlor, and 2,4-D, are regulated by CONAMA Resolution No. 357, meaning that they have maximum allowable values in water under Brazilian legislation. Although these pesticides are regulated in Brazil, they are not necessarily monitored regularly nationwide, and compliance with individual regulatory thresholds does not imply the complete absence of ecological risk. Among the detected pesticides, 2,4-D, imidacloprid, thiamethoxam, fipronil, tebuconazole, azoxystrobin, trifloxystrobin, propiconazole, epoxiconazole, and metolachlor have recent documentation of use, registration, or technical association with rice cultivation, particularly in irrigated rice systems (Ministério da Agricultura, Pecuária e Abastecimento [MAPA], 2021; Andres et al., 2022; Sociedade Sul-Brasileira de Arroz Irrigado [SOSBAI], 2022; Agência de Defesa Agropecuária e Florestal do Estado do Amazonas [ADAF], 2024; Audeh et al., 2025).

Although carbofuran and carbendazim were detected, their use is currently prohibited in Brazil; carbofuran has been banned for rice cultivation since 2017, and carbendazim was prohibited by RDC No. 739/2022 (Agência Nacional de Vigilância Sanitária [ANVISA], 2018, 2022, 2025).

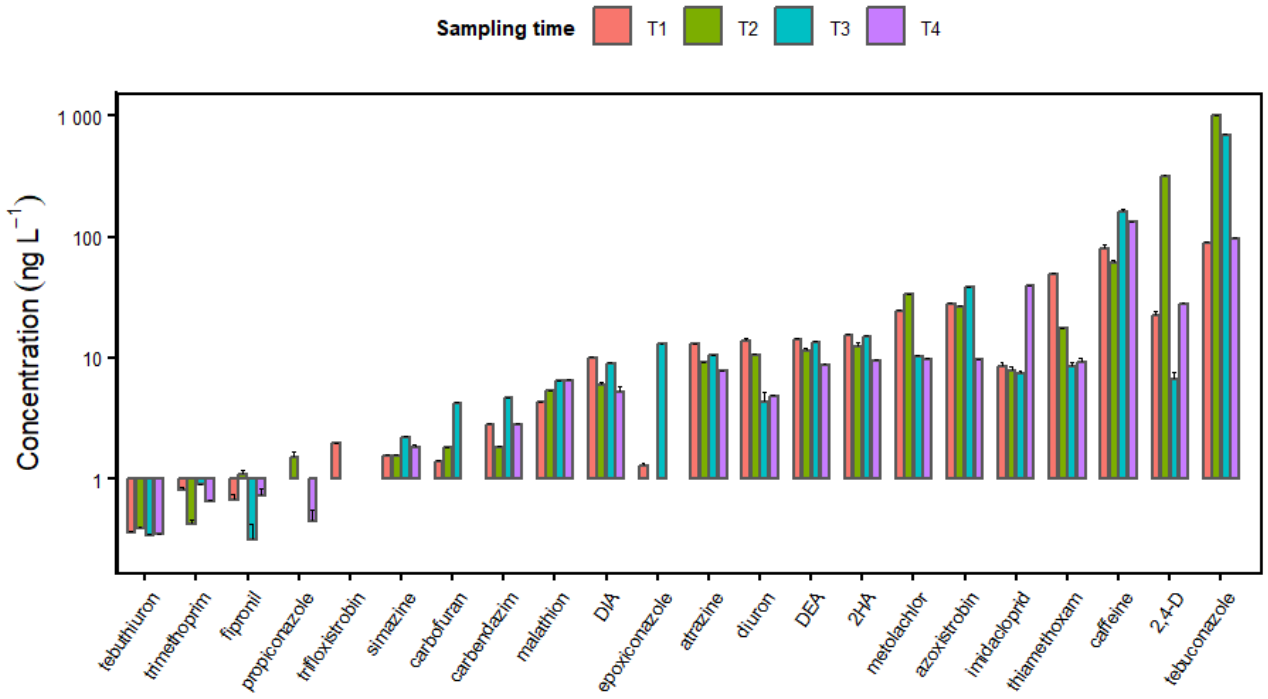


Fig. 3 Average concentrations of contaminants detected in surface water samples from Lagoa Mirim throughout the four sampling times. T1 and T2 correspond to the irrigation period of the rice crops, T3 represents the water drainage period before harvest, and T4 corresponds to the off-season. The bars represent mean ± standard deviation. DIA, DEA, and 2HA correspond, respectively, to the triazine metabolites deisopropylatrazine, desethylatrazine, and 2-hydroxyatrazine

The compounds showed marked differences among sampling periods and among the concentrations detected. T1 and T2 correspond to the rice field irrigation period, when there is greater water withdrawal from Mirim Lagoon. T3 represents an especially relevant period, as it is associated with the drainage of water used in the fields before harvest, which may favor the return of agricultural residues to the lagoon. T4 corresponds to the off-season; therefore, the presence of compounds during this period may indicate environmental persistence or sources not directly related to recent agricultural management. T1 was the period with the highest number of detected compounds, followed by T2 and T3, which showed very similar values. T4 had the lowest number of compounds, although several detections were still recorded during the off-season. Compounds such as tebuconazole, 2,4-D, caffeine, and thiamethoxam stood out for presenting the highest mean concentrations throughout the monitoring period. In contrast, compounds such as tebuthiuron and trimethoprim occurred at lower concentrations and more sporadically. Epoxiconazole, propiconazole, and trifloxystrobin showed seasonal occurrence, being detected only in specific periods (Fig. 3). In addition, temporal variations indicate seasonal influence and a possible relationship with agricultural activities and anthropogenic inputs in the Mirim Lagoon watershed.

Principal Component Analysis (PCA) did not show a clear separation among sampling periods, indicating the absence of well-defined spatial or temporal patterns in the distribution of emerging contaminants in Mirim Lagoon (Fig. 4). The first two axes explained 40.6% of the total variance in the data, with 25% represented by axis 1 and 15.6% by axis 2. A high overlap was observed among samples from different periods, suggesting similarity in contaminant composition throughout the monitoring

period. Compounds such as caffeine, 2,4-D, and malathion showed greater association with some specific samples, whereas other contaminants remained more homogeneously distributed among periods.

Permutational multivariate analysis of variance (PERMANOVA) corroborated the patterns observed in the PCA, indicating no significant difference in contaminant composition among sampling periods ($R^2 = 0.19$; $p = 0.091$). Although the sampling period explained 19% of the total variation in the data, the results were not statistically significant ($p > 0.05$), suggesting that there was no evident temporal influence of rice management on emerging contaminant concentrations in Mirim Lagoon during the evaluated period.

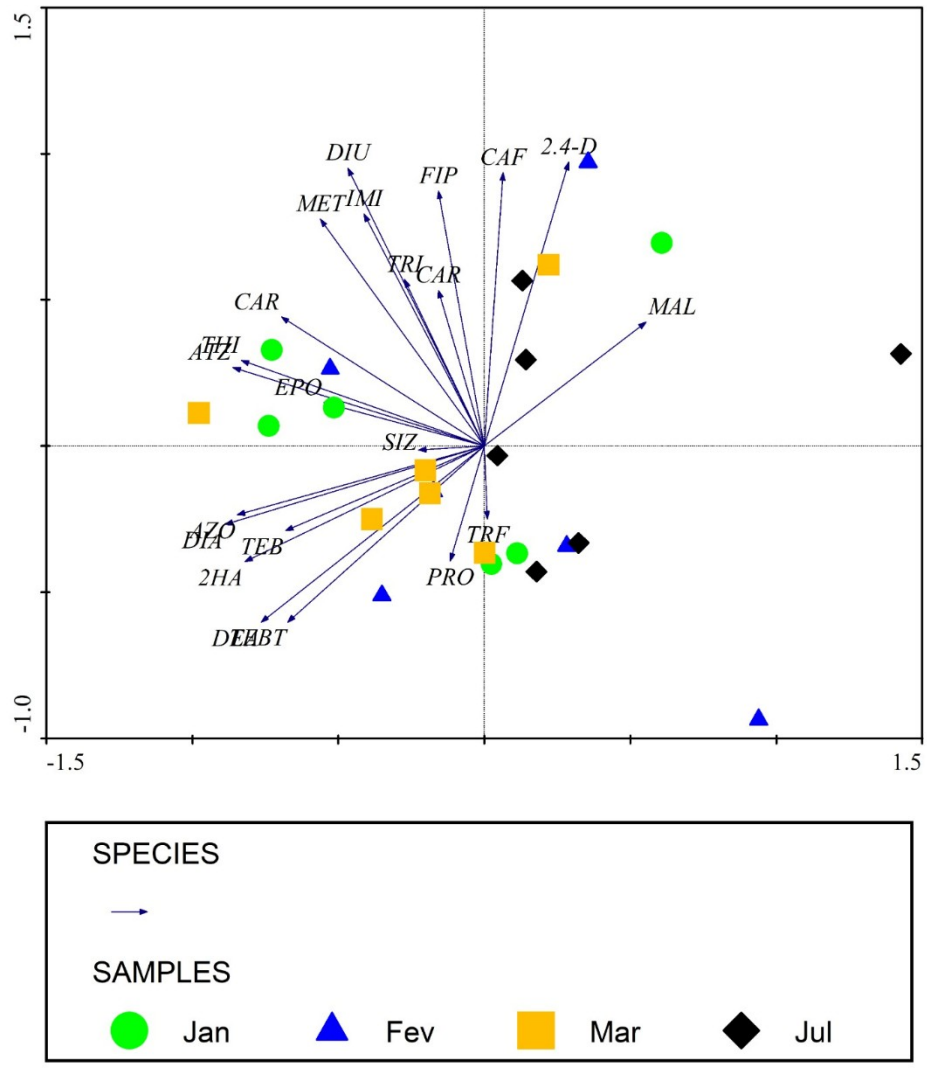


Fig. 4 Principal Component Analysis (PCA) of the composition of emerging contaminants detected in water samples from Lagoa Mirim during sampling periods T1 to T4. T1 and T2 correspond to the irrigation period of rice crops, T3 represents the water drainage period before harvest, and T4 corresponds to the off-season. Axes 1 and 2 explained 25% and 15.6% of the total variance of the data, respectively. DIA, DEA, and 2HA correspond, respectively, to the triazine metabolites deisopropylatrazine, desethylatrazine, and 2-hydroxyatrazine.

In the present study, 22 compounds were detected among 26 analyzed, indicating widespread occurrence of contaminants in the surface waters of Mirim Lagoon. Considering the highest concentrations observed, tebuconazole stood out, followed by 2,4-

D, caffeine, and thiamethoxam. Compounds such as tebuthiuron, trimethoprim, and fipronil occurred at lower concentrations and more sporadically. These detections show that the observed contamination involved a diversity of chemical groups, including herbicides, fungicides, insecticides, herbicide metabolites, and compounds associated with anthropogenic activity, such as caffeine.

In Brazil, maximum permitted values for several pesticides in water intended for human consumption are established by Ordinance GM/MS No. 888/2021. However, for surface waters, the number of pesticides and their respective maximum permitted values in these systems represents only a small fraction, mainly through CONAMA Resolution No. 357/2005. Thus, many pesticides detected in aquatic environments do not have specific ecological water quality standards for Brazilian surface waters. Therefore, their levels in surface waters are often compared with the maximum admissible concentrations (MACs) established for water intended for human consumption in Europe, which are 100 ng L^{-1} for individual pesticides and 500 ng L^{-1} for total pesticides (European Union, 2020).

Considering that Lagoa Mirim is classified as a Class 2 freshwater body according to CONAMA Resolution No. 357/2005, the compounds detected in this study that are regulated by this legislation were atrazine, simazine, malathion, metolachlor, and 2,4-D. The maximum concentrations established by CONAMA for these compounds are 2, 2, 0.1, 10, and 4 µg/L, respectively. Regarding these regulated compounds, none exceeded the permitted standard. However, several other detected compounds, including DIA, 2HA, DEA, ametryn, caffeine, imidacloprid, hexazinone, diuron, tebuconazole, epoxiconazole, propiconazole, profenofos, chlorpyrifos, trimethoprim, thiamethoxam, tebuthiuron, azoxystrobin, trifloxystrobin, and fipronil, do not have specific limits under CONAMA Resolution No. 357/2005. This limits the regulatory assessment of contamination by pesticides, transformation products, and other emerging contaminants in Brazilian surface waters.

Comparing the results with the MACs established in Europe for water intended for human consumption, five pesticides exceeded the individual limit of 100 ng L^{-1}: tebuconazole, 2,4-D, imidacloprid, thiamethoxam, and azoxystrobin. The greatest exceedance was observed for tebuconazole, which reached 4,999.39 ng L^{-1}, which indicates that pesticide contamination in Lagoa Mirim may reach levels exceeding the international reference values used for the protection of drinking water. In addition to reference values for drinking water, the European Union establishes Environmental Quality Standards (EQS) for priority substances in surface waters. These standards include annual average EQS (AA-EQS), related to chronic exposure, and maximum allowable concentration EQS (MAC-EQS), related to short-term exposure peaks. Among the pesticides detected in the present study, some appear on the WFD lists of priority/monitored substances, such as atrazine, simazine, diuron, and chlorpyrifos. However, the remaining pesticides detected in this study also lack EU EQS for inland surface waters (European Parliament and Council of the European Union, 2008).

Comparing the present study with the study that provided the first detailed analysis of the influence of pesticides on water quality in areas adjacent to Mirim Lagoon (Corrêa et al., 2022), tebuconazole, imidacloprid, and atrazine were the pesticides detected in both studies. Corrêa et al. (2022) quantified twenty-four compounds in lagoon samples, which were mainly associated with irrigated rice cultivation activities. Montagner et al. (2019) also found caffeine and atrazine in water samples during 10 years of monitoring emerging contaminants in drinking water, surface water, groundwater, and effluents in the state of São Paulo. The two main contaminants detected in surface waters were caffeine (97%) and atrazine (69%). Montagner et al. (2019) identified caffeine, atrazine, carbendazim, fipronil, malathion, and imidacloprid as compounds of greater concern in waters from the state of São Paulo, due to their high detection frequency and detection above water quality criteria. These same compounds were also detected in the present study, indicating that Mirim Lagoon contains contaminants already recognized as relevant in other Brazilian aquatic systems.

Tebuconazole is a triazole fungicide widely used in vegetables, cereals, fruits, and legumes to control fungal diseases. Its mode of action is the inhibition of ergosterol biosynthesis, which is an essential component of fungal cell membranes (Shcherbakova et al., 2021). This fungicide is one of the pesticides recognized for its efficacy and persistence; its environmental half-life in soil ranges from 400 to 600 days (Lewis et al., 2016; Cui et al., 2018), which has contributed to its use on a global scale (Klingelhöfer et al., 2022). It is also recognized for its frequent detection in aquatic environments through surface runoff, with maximum reported concentrations of up to 180 μg L^{-1} in Brazil, 1.8 μg L^{-1} in the United States, and 0.133 μg L^{-1} in China (Brovini et al., 2023; Glinski et al., 2018; Peng et al., 2018). In addition, it has been associated with potential ecotoxicological effects on non-target organisms, such as fish (Carnib et al., 2025), amphibians (Ihle et al., 2025), and may also affect primary producers, including aquatic macrophytes (Mohr et al., 2025) and algae (Queirós et al., 2023). The highest concentration of tebuconazole was recorded in T2, reaching 4999.4 ± 47.1 μg/L at site P3, an area with greater rural and agricultural influence.

The herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) is used to control weeds in rice, oats, coffee, sugarcane, rye, barley, corn, pastures, soybean, sorghum, and wheat (ANVISA, 2022). It has been one of the most widely used herbicides in Brazil and worldwide over the last two decades. Recent studies have demonstrated the occurrence of 2,4-D in surface waters from different agricultural regions, including Brazil, Canada, Europe, Argentina, and Uganda, often associated with pesticide mixtures and potential risks to aquatic organisms (Goulart et al., 2024; Feng et al., 2024; Navarro et al., 2024; Oltramare et al., 2023). In mesocosms, the persistence of 2,4-D in water and sediment was observed, and high environmental risk was estimated, with risk quotient values for 2,4-D reaching up to 1359 in freshwater and 98 in sediment (Goulart et al., 2024). The highest concentration of 2,4-D was recorded in T2, reaching 628.4 ± 12.7 μg/L at site P1, an area with greater rural and agricultural influence.

In the present study, caffeine showed its maximum concentration in T3, at site P4, an area characterized by local occupation and recreational use, reaching 618.00 ± 36.87 μg/L. Researchers have documented the presence of caffeine in surface waters, groundwater, and even in water sources intended for human consumption worldwide. The main sources of caffeine input into these environments are human consumption, excretion only 3% of the ingested amount is excreted unchanged in urine and the inadequate disposal of effluents (Gardinali & Zhao, 2002). Sewage contamination, especially in regions with inadequate wastewater treatment systems, is the main cause of its occurrence, since high caffeine concentrations are found near urban centers (Vieira et al., 2021). Caffeine is a highly soluble compound that is stable in water and generally occurs at high concentrations, up to mg/L levels, in sewage. It is only partially removed by wastewater treatment plants, meaning that conventional treatment systems do not completely remove this compound (INCTAA, 2014). Ozaki et al. (2024) demonstrated that caffeine concentrations in urban drainage systems tended to increase with the age of the sewer network. In areas with sewer systems older than 40 years, caffeine concentrations were at least two orders of magnitude higher than those observed in systems approximately 10 years old.

Thiamethoxam, a neonicotinoid insecticide, has been commonly applied in agriculture to control whiteflies, aphids, among others (El-Naggar et al., 2013). It acts on the nervous system by blocking postsynaptic acetylcholine receptors, leading to paralysis and death of target organisms (Fouad & Abdel-Raheem, 2024). It has been found in surface waters and reservoirs and has the potential to pose risks to aquatic organisms, especially invertebrates and fish. Behavioral changes, neurotoxicity, oxidative stress, and metabolic disturbances have been observed in aquatic organisms (Sun et al., 2025; Yang et al., 2023). The maximum concentration of thiamethoxam observed in this study was 179.1 ± 4.2 μg/L, recorded in T1 at site P5, an area with greater rural and agricultural influence.

Imidacloprid, another widely used neonicotinoid insecticide, is also recognized for its efficacy and environmental persistence. It has a 50% dissipation time (DT50) of 27 to 180 days under field conditions (Brown et al., 2025). Through surface runoff, imidacloprid is commonly detected at concentrations ranging from 0.001 μg/L (> LOD) to 320 μg/L worldwide (Van Dijk et al., 2013). In the present study, the maximum concentration of imidacloprid observed was 180.5 ± 2.7 μg/L, recorded in T4 at

site P3, an area with greater rural and agricultural influence. These values remained within the environmental range previously reported for Brazilian ecosystems, which varies from 0.01 µg/L (Gonçalves et al., 2020) to 3.65 µg/L (Becker et al., 2009). Global cases of water pollution by imidacloprid are concerning due to the toxic effects that this insecticide can cause in aquatic organisms (Queiroz et al., 2022). In the study by Velásquez and Bautista (2025), reduced body length and total immobility were demonstrated in tadpoles; imidacloprid may also alter algal growth under aquatic contamination scenarios (Lozano et al., 2025).

The detection of various pesticides in the Lagoa Mirim watershed compounds used or registered for irrigated rice cultivation warrants attention, given that irrigated rice is a major agricultural activity in southern Rio Grande do Sul and was identified within the 5 km buffer zones surrounding all sampling points in this study. Consequently, the detection of compounds such as 2,4-D, imidacloprid, thiamethoxam, fipronil, tebuconazole, azoxystrobin, trifloxystrobin, propiconazole, epoxiconazole, and metolachlor aligns with the regional agricultural context, although their occurrence cannot be attributed solely to rice cultivation. This interpretation was supported by PCA, which did not show clear groupings of samples based on sampling locations or periods, and by PERMANOVA, which did not indicate a significant difference in the composition of contaminants between the sampled periods ($R^2 = 0.19$; $p = 0.091$). In summary, the results indicate that, although certain compounds stood out in specific periods, the occurrence of emerging contaminants varied between sampling locations and times, without the formation of a well-defined spatial or temporal pattern. In contrast, in the study by Corrêa et al. (2022), it was possible to link the results to seasonality, as the authors observed temporal patterns related to the phases of irrigated rice cultivation, especially for herbicides and fungicides.

The absence of a temporal or spatial pattern in the composition of emerging contaminants in the present study may be related to the hydroclimatic and/or hydrodynamic conditions of Lagoa Mirim, specifically its large surface area and high mixing capacity which can facilitate the dilution and dispersion of these contaminants throughout the aquatic system. The regional climate is classified as humid subtropical with hot summers, characterized by average temperatures exceeding 22°C during the warmest months and falling below 18°C during the coldest months, with an average annual precipitation of approximately 1,450 mm (Alvares et al., 2013; Cardoso et al., 2024). These climatic characteristics can influence the seasonal dynamics of Lagoa Mirim, affecting surface runoff, dilution capacity, water temperature, and the transport of contaminants from agricultural areas to aquatic environments. Gomes Jr. et al. (2023) highlighted the influence of mixing, transport, and surface runoff processes on the fate and spatial distribution of contaminants in aquatic systems.

Thus, even though the samples from Mirim Lagoon were collected during periods associated with irrigated rice management, the contaminants may remain persistently or relatively homogeneously distributed in this aquatic system. This could be observed because almost all compounds were detected in T4, a period selected for water sampling because it corresponds to a time with little or no agricultural activity and was considered a period of lower contribution of agricultural residues. Therefore, it is important to highlight the half-lives of the compounds detected during the off-season (T4), especially those that stood out due to their higher concentrations, such as tebuconazole, 2,4-D, caffeine, thiamethoxam, and imidacloprid. Tebuconazole is stable to hydrolysis in water, with a half-life greater than one year, and shows slow degradation by photolysis, with an estimated half-life of approximately 590 days (FAO/WHO, 1994). The half-life of 2,4-D in aquatic systems with oxygen availability has been reported to be approximately 15 days; under conditions of low oxygen availability, its half-life ranges from 41 to 333 days (ATSDR, 2020). Caffeine is exceptionally stable, with a reported half-life of 100 to 240 days (Hillebrand et al., 2012). For thiamethoxam, its half-life has been reported to range from 8 to 16 days under aerobic conditions and from 24 to 44 days under anaerobic conditions (Uğurlu et al., 2015). For imidacloprid, its temperature- and moisture-normalized DT50 values (20 °C and 10 kPa soil moisture) ranged from 99 to 129 days under laboratory conditions and from 27 to 180 days under field conditions (Brown et al., 2025).

The results also suggest the simultaneous influence of multiple anthropogenic sources of contamination in the watershed, including agricultural activities, urban areas, and domestic effluent discharge. In addition to pesticides, caffeine, coliforms, and nutrients (total phosphorus and total nitrogen) were also found, which makes it difficult to identify a pattern exclusively related to irrigated rice cultivation. Recent studies have shown that these aquatic environments are subject to anthropogenic contaminants and often receive contaminants from multiple sources simultaneously, through agricultural runoff, crop drainage, and domestic effluent discharge (Santos et al., 2022; Ozaki et al., 2024; Ramalho et al., 2025). For example, in the study by Xiang et al. (2025), the authors observed the concomitant occurrence of agricultural residues and compounds associated with domestic wastewater in reservoirs used for public water supply, demonstrating the complexity of diffuse contamination sources in aquatic environments.

Conclusions

This study presents an updated assessment of environmental contaminants and water quality conditions in the Lagoa Mirim watershed, integrating field monitoring (T1–T4) with a systematic review of available literature. The detection of 22 out of the 26 analyzed compounds demonstrates the widespread occurrence of pesticides, herbicide metabolites, caffeine, and an antibiotic in the surface waters of this transboundary system. Several detected compounds—including tebuconazole, 2,4-D, thiamethoxam, and caffeine—showed high concentrations and frequent occurrence, indicating the presence of substances associated with both agricultural activities and urban/domestic sources.

Comparison with Brazilian and European regulatory guidelines revealed significant gaps in surface water monitoring. Although pesticides regulated by CONAMA Resolution No. 357/2005 did not exceed Brazilian limits, several detected contaminants lack specific ecological standards for surface waters in Brazil. This regulatory limitation hinders the assessment of potential ecological risks associated with emerging contaminants in aquatic systems such as Lagoa Mirim.

The analyses did not reveal well-defined temporal or spatial patterns in contaminant composition across the sampling periods. This suggests the influence of multiple sources, environmental persistence, and hydrodynamic dispersion within the lagoon—factors that may contribute to the influx and persistence of contaminants in this system.

Physicochemical and microbiological parameters also raised environmental concerns. Certain parameters exceeded legal limits at specific locations, particularly those most affected by urbanization, recreational activities, or domestic sewage inputs. These results reinforce that water quality in Lagoa Mirim is impacted by multiple pressures, including agricultural runoff, nutrient enrichment, and fecal contamination.

Finally, the systematic review confirmed that studies on environmental contaminants in the Lagoa Mirim watershed remain scarce and still focus primarily on conventional water quality parameters and metals. Thus, this study expands existing knowledge by providing new information on emerging contaminants and the lack of more comprehensive regulatory standards in a strategic transboundary watershed. These results underscore the need for continuous monitoring and the broader inclusion of emerging contaminants in water quality programs.

Declarations

All authors have read, understood, and complied, as applicable, with the statement on “Ethical responsibilities of authors” found in the Instructions for Authors.

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Competing Interests

The authors have no relevant financial or non-financial interests to declare.

Author Contributions

All authors contributed to the study conception and design. Field sampling, data organization, investigation, and the first draft of the manuscript were performed by Karen Pinheiro Lackman. Mariana Amaral Dias was responsible for the methodology, chemical analysis, chromatographic analysis, and data validation. Cassiana Carolina Montagner contributed to the supervision of chemical analyses, methodology, resources, data validation, and manuscript revision. Camila de Martinez Gaspar Martins and Raquel Aparecida Moreira contributed to conceptualization, supervision, resources, methodology, data interpretation, and manuscript revision. All authors commented on previous versions of the manuscript and read and approved the final version.

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Supplementary Material

Environmental contaminants in a strategic transboundary watershed: a systematic review and occurrence assessment in Lagoa Mirim (Southern Brazil)

Table S1. Characteristics and main findings of studies included in the qualitative synthesis of environmental quality in Mirim Lagoon.

Category	Reference	Study design and spatial scope	Matrix, variables and analytical approach	Main quantitative results	Main interpretation and critical notes
Water quality	Fia et al. (2009)	Water; monitoring stations in the Mirim Lagoon basin. Only sites located in the lagoon were retained.	Surface-water sampling; pH, temperature, DO, BOD, total P, total N, turbidity, total solids, chlorophyll-a and thermotolerant coliforms; trophic-state assessment.	Lagoon sites showed elevated phosphorus and trophic conditions ranging from mesotrophic to hypereutrophic depending on site/date.	Agricultural nutrient inputs and local organic contamination were identified as important pressures. Basin tributary results were not used in the present synthesis.
Water quality	Pinto et al. (2020)	Five-year database supplied by the Mirim Lagoon Development Agency; seasonal comparison of monitoring sites in Mirim Lagoon.	Routine physicochemical and microbiological parameters; descriptive statistics and discriminant analysis.	Seasonal discrimination was driven principally by variables related to temperature, oxygen, nutrients, solids/turbidity and microbiological contamination; the article evaluates database values rather than a new sampling campaign.	Climatic seasonality affected the multivariate water-quality pattern. Dataset overlaps the ALM monitoring series used in several subsequent studies.
Water quality	Drose et al. (2020)	Water samples from monitoring points distributed along Mirim Lagoon; ALM monitoring dataset.	Water-quality variables evaluated jointly by principal component analysis (PCA).	The retained components grouped variables associated with organic pollution and variables associated with soil/rock particles, solids and phosphorus.	Anthropogenic organic inputs and diffuse agricultural/mineral sources were the main interpreted pressure groups. This is a reanalysis of monitoring data, not an independent campaign.
Water quality	Valentini et al. (2020)	Mirim Lagoon monitoring points; ALM historical dataset.	Standard WQI variables and statistical/multivariate interpretation.	Water-quality classes varied among sites and sampling dates; phosphorus, solids/turbidity, DO and thermotolerant coliforms were prominent drivers.	Indicated influences from agricultural activity and organic contamination. Dataset overlaps other Valentini/Borges monitoring studies.
Water quality	Valentini et al. (2021a)	Mirim Lagoon; 154 complete observations from the ALM monitoring database.	Original CETESB WQI; Pearson/Spearman correlations; multiple linear regression.	A three-variable model using total phosphorus, DO and thermotolerant coliforms explained 72.8% of WQI variation ($R^2 = 0.728$).	Proposed a simplified WQI equation. Results represent statistical modelling of an existing monitoring database.
Water quality	Valentini et al. (2021b)	Mirim Lagoon monitoring sites; historical ALM water-quality records.	Nine CETESB-WQI parameters; normality tests and Pearson/Spearman correlation analysis.	Total phosphorus showed the strongest and most consistent influence on final WQI; thermotolerant coliforms, DO, turbidity and total solids also contributed.	Reinforced nutrient and organic-pollution pressures; substantial data overlap with Valentini et al. (2021a) and Borges et al. (2023).
Water quality	da Silveira et al. (2021)	Four São Gonçalo Channel sites and six direct Mirim Lagoon sites (LM1–LM6); monthly campaigns from April 2018 to April 2019. Only LM sites were retained.	Temperature, DO, pH, BOD, TN, TP, turbidity, total solids, thermotolerant coliforms and chlorophyll-a; CETESB WQI, trophic-state index and statistical analyses.	At LM sites, TP ranged from 0 to 2.09 mg L^{-1}, chlorophyll-a from approximately 0.27 to 40.42 µg L^{-1}, and thermotolerant coliforms from 0 to >1,600 MPN 100 mL^{-1}.	Water quality varied spatially and temporally; phosphorus and microbiological contamination were recurrent limitations. São Gonçalo Channel values were excluded.
Water quality	Caballero et al. (2022)	River–lake transition and Mirim Lagoon; field measurements paired with Sentinel-2 MSI imagery. Direct lagoon observations retained.	Chlorophyll-a and optical/physicochemical variables; empirical and semi-empirical remote-sensing models using Sentinel-2 bands.	The best-performing spectral formulations produced significant chlorophyll-a estimates, but accuracy depended on optical complexity and river–lake transition conditions.	Demonstrated the potential and limitations of satellite monitoring of chlorophyll-a in Mirim Lagoon.
Water quality	Caballero (2023)	Mirim Lagoon; in situ turbidity observations paired with Sentinel-2 imagery.	Turbidity measured by standard nephelometric procedures; atmospheric correction and empirical predictive modelling with Sentinel-2 reflectance.	The selected spectral model showed a significant relationship with measured turbidity and enabled spatial mapping of lagoon turbidity.	Remote sensing can complement field monitoring, but performance depends on image/sampling coincidence and atmospheric correction.
Water quality	Borges et al. (2023)	Seven direct lagoon sites (ML1–ML7); monitoring from 2018–2022, with 17 complete months used.	Temperature, DO, pH, BOD, TN, TP, turbidity, total solids and thermotolerant coliforms; APHA methods; CETESB and simplified WQIs; paired t tests.	Temperature 6.6–32.1 °C; DO 3.61–10.34 mg L^{-1}; pH 5.30–9.00; BOD 0–5.24 mg L^{-1}; TN 0–2.51 mg L^{-1}; TP 0–3.50 mg L^{-1}; turbidity 7.17–208 NTU; total solids 101–409 mg L^{-1}; coliforms 0–14,000 MPN 100 mL^{-1}. CETESB WQI 58.3–81; simplified WQI 48.0–76.9.	TP was most influential at ML1–ML5 and coliforms at ML6–ML7. No site-level difference between WQI formulations ($p > 0.05$). Published version: Water Air Soil Pollut 234, 742.
Water quality	Silva et al. (2024)	January, March and June 2022. Direct lagoon sites P6, P8, P9, P11 and P12 retained; tributary P4 excluded.	Physicochemical and microbiological parameters; toxicity tests with Pseudopediastrum boryanum, Ceriodaphnia dubia, Daphnia magna and Danio rerio; behavior, AChE, GST, IBR, PERMANOVA and RDA.	Temperature 9.0–31.5 °C; DO 5.67–9.27 mg L^{-1}; conductivity 66–382 µS cm^{-1}; pH 7.6–9.1; turbidity 7.9–58.3 NTU; solids 116.5–344.0 mg L^{-1}; TP ND–1.57 mg L^{-1}; TN 0.08–0.34 mg L^{-1}; BOD 0.10–3.20 mg L^{-1}; coliforms 6.1–1,600 MPN 100 mL^{-1}; chlorophyll-a 2.17–31.65 µg L^{-1}.	March produced the strongest integrated biomarker response. Period explained more variation than site. Supplementary TP/TN detection limits conflict with some reported values; this inconsistency is noted rather than corrected.
Heavy metals	Niencheski et al. (2001)	Eight fish from northern Mirim Lagoon in September 1998: two Micropogonias furnieri and six Odontesthes bonariensis.	Total Hg and methyl-Hg in muscle; acid digestion and cold-vapor atomic fluorescence. LODs: 1 ng g^{-1} wet weight (total Hg) and 0.1 ng g^{-1} (methyl-Hg).	Individual values were shown graphically; all were below 0.5 µg g^{-1} wet weight. Hg was almost entirely methylated.	Hg increased with fish length ($p < 0.01$). Mirim fish generally had lower concentrations than similarly sized Patos Lagoon fish. Small sample size (n = 8).
Heavy metals	Santos et al. (2003)	Surface sediments collected in September 2001. Twenty-two lagoon sites; Canal São Gonçalo and Jaguarão River sites excluded. Metal dataset available for 20 samples.	<63 µm fraction; aqua regia + HF digestion. Cr, Cu, Zn, Fe and Mn by flame AAS; Cd and Pb by graphite-furnace AAS.	Mean ± SD (range), mg kg^{-1}: Cd 0.05 ± 0.03 (0.01–0.12); Pb 4.4 ± 1.2 (1.6–6.5); Cu 12.7 ± 3.4 (5.6–18.7); Zn 55.9 ± 17.6 (24.8–99.0); Cr 14.4 ± 3.3 (8.7–19.6); Mn 288.4 ± 138.5 (27.5–575); Fe 1.89 ± 0.61% (0.9–3.1%).	No evidence of anthropogenic enrichment. Fe/Cu/Zn/Mn/Cr were higher in the south; Pb was higher in the north; Cd was broadly distributed.
Heavy metals	Mirlean et al. (2003)	Fifteen surface-sediment samples collected in Mirim Lagoon in 2001; upper 10 cm sampled with a Van Veen grab.	Labile As: 1 mol L^{-1} HCl extraction for 24 h. Total As: HF/aqua-regia digestion. Hydride-generation flame AAS.	Labile As 0.1–0.6 mg kg^{-1} (mean 0.3 ± 0.14); total As 0.6–4.4 mg kg^{-1} (mean 2.5 ± 1.1). Labile fraction 8.5–21.4% (mean 14.1%).	Mirim had background/low As concentrations; the severe contamination discussed in the paper occurred in the Patos Lagoon estuary, not Mirim Lagoon.
Heavy metals	Friedrich et al. (2006)	Water collected across Mirim Lagoon; dissolved and suspended particulate fractions.	Dissolved Cu, Cr, Zn, Pb, Ni, Cd, Fe, Mn, Al, Hg and As; particulate Cu, Cr, Zn, Pb, Ni, Cd, Fe, Mn and Al; atomic-spectrometric determinations and geochemical normalization.	Complete numerical ranges are not reproduced in the accessible article record; authors reported generally low concentrations, with Zn and Cd requiring further investigation.	Meteorological and hydrodynamic processes exceeded identifiable anthropogenic effects. Fe was the main particulate carrier and a better normalizer than Al.

Category	Reference	Study design and spatial scope	Matrix, variables and analytical approach	Main quantitative results	Main interpretation and critical notes
Heavy metals	Bueno et al. (2025)	Three Mirim Lagoon sediment cores (MIR1–MIR3), collected October 2006–January 2008; dated using ^{210}Pb/^{226}Ra.	Instrumental neutron activation analysis of 25 major, trace and rare-earth elements; enrichment factors normalized to Sc; La–Sc–Th provenance analysis.	MIR1/MIR2/MIR3 ranges (mg kg^{-1}): Ba 211–527/729–1,354/475–732; Ce 71–97/71–88/59–84; La 31–44/33–40/27–39; Th 9.2–16.2/9.2–14.3/8.9–13.5; U 2.6–3.6/2.4–3.4/2.4–3.9; Fe 1.2–3.4/1.4–2.7/1.2–2.6%.	Mirim sediments showed granitic provenance and Ba enrichment (EF near 2 in MIR1 and near 3 in MIR2), associated with Candiota coal mining/combustion. Elemental data are original; chronology overlaps Bueno et al. (2021).
Pesticides/ agricultural pressure	Bueno et al. (2021)	Dated sediment cores from Mirim Lagoon and connected regional systems; palaeolimnological reconstruction of land-use and hydrological change.	Sediment chronology, sedimentation rates and multiple palaeoenvironmental/geochemical proxies; historical land-use and economic records.	Following the 1977 water-locking intervention, sedimentation increased from approximately 0.25 cm yr^{-1} under predisturbance conditions to >1 cm yr^{-1}. No pesticide residues were quantified.	Documents agricultural intensification and hydrological transformation, not pesticide occurrence. It should be described as agricultural pressure/land-use change rather than pesticide quantification.
Pesticides	Corrêa et al. (2022)	Five campaigns (Dec 2018–Mar 2019) in three Mirim Lagoon tributaries: Chasqueiro (P2), Canhada (P3) and Arroio Grande (P4); Chasqueiro Dam (P1) was also sampled.	Surface water (20 cm); filtration, C18 solid-phase extraction and LC–ESI–MS/MS (SRM). Ninety-seven pesticides investigated; LOQs 0.004–0.8 µg L^{-1}.	Twenty-four pesticides detected. Frequencies: azoxystrobin and tricyclazole 78%; imazethapyr 72%; tebuconazole and thiamethoxam 67%; bentazone and imazapic 61%. Ranges (µg L^{-1}): azoxystrobin <0.008–6.672; bentazone 0.056–1,003.42; clomazone 0.15–8.68; imazethapyr 0.037–3.61; quinclorac <0.8–2,296.36; tebuconazole 0.011–1.27; thiamethoxam <0.008–5.15; tricyclazole 0.018–1,409.78. P2/P3 contained 21/22 pesticides; maximum summed concentrations 3,343.18/3,487.02 µg L^{-1}. P4 contained 19 pesticides.	The tributaries are potential agricultural input pathways to Mirim Lagoon; values were not measured in the lagoon itself. P1 had 7 compounds at ≤0.112 µg L^{-1}. No regulated pesticide exceeded the Brazilian MAC adopted by the authors. The impossible imidacloprid mean reported in Table 3 (1.00 µg L^{-1} vs maximum 0.25 µg L^{-1}) was not reproduced.
Emerging contaminants	Alves et al. (2023)	Dated sediment cores from Mirim Lagoon used to reconstruct the historical appearance of microplastics.	Density separation, microscopic identification and polymer characterization; sediment chronology used to relate first occurrence to the Anthropocene.	Microplastics occurred in dated sediment layers; rayon, PVC and acrylate were among the most commonly identified polymers. Concentrations and polymer distributions varied with depth/core.	Proposed microplastics as a chronological marker. Study concerns sedimentary microplastics, not dissolved contaminants in current lagoon water.

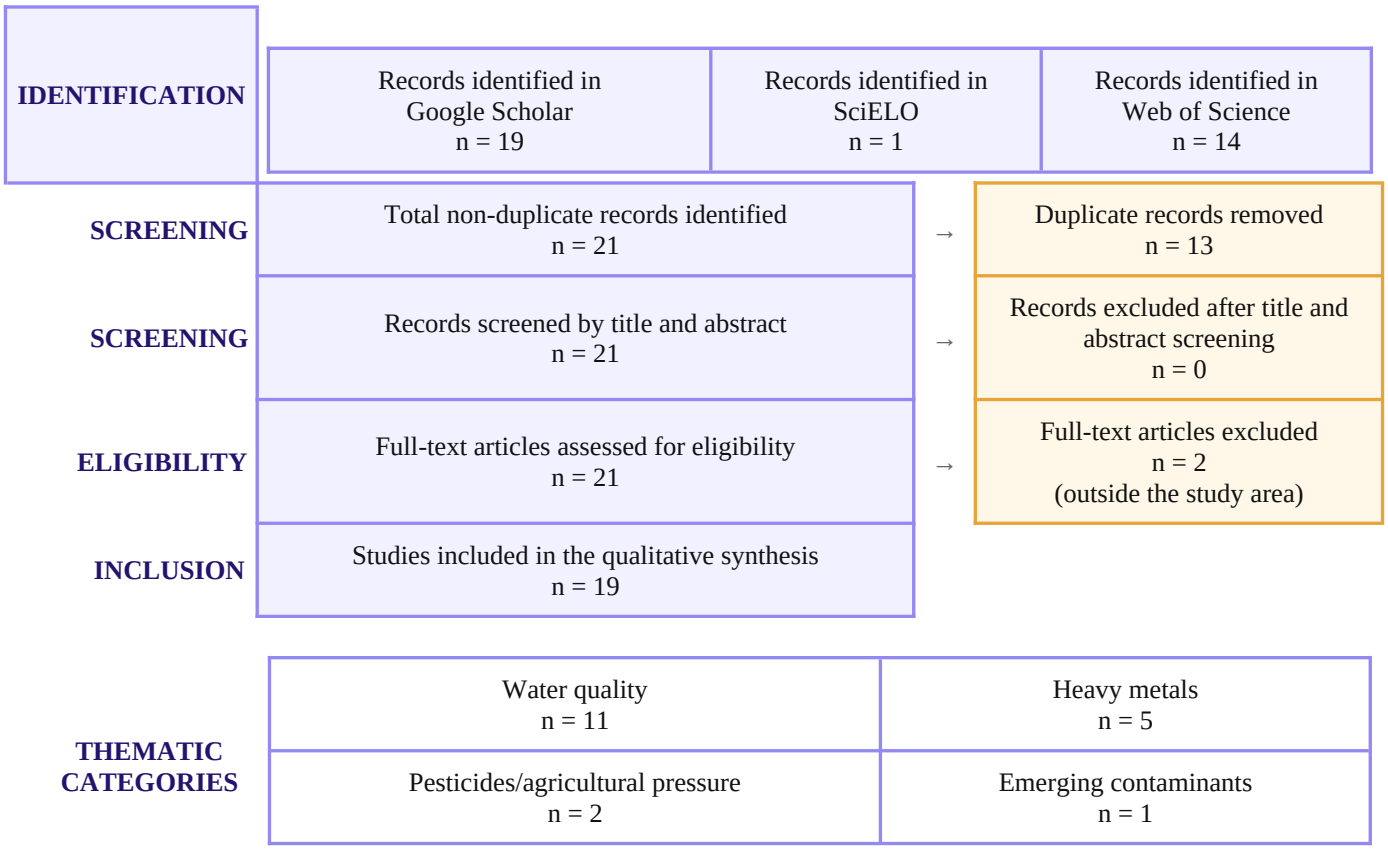


Fig. S1. Flowchart of the systematic literature review process used to identify peer-reviewed studies on water quality and environmental contaminants in the Mirim Lagoon watershed. Records were obtained from Google Scholar, SciELO, and Web of Science. Of the 34 records identified, 13 duplicates were removed. Twenty-one full-text articles were assessed, two were excluded because they were outside the study area, and 19 studies were included in the qualitative synthesis: water quality (n = 11), heavy metals (n = 5), pesticides and agricultural pressure (n = 2), and emerging contaminants (n = 1).

Table S2. Decision matrix applied during the systematic literature review for study screening, eligibility assessment, and final inclusion. Inclusion and exclusion criteria were predefined to ensure transparency and reproducibility in selecting studies addressing water quality, environmental contaminants, and relevant agricultural pressure in Mirim Lagoon and its hydrologically connected watershed.

Step	Decision criterion	Inclusion decision	Exclusion decision	Exclusion code
1	Publication type	Peer-reviewed scientific article	Thesis, dissertation, technical report, conference abstract, book chapter, institutional document or non-peer-reviewed material	E1
2	Publication period	Published between 2001 and 2025	Published before 2001 or after 2025	E2
3	Study area and hydrological connection	Conducted in Mirim Lagoon (Laguna Merín), its watershed, or tributaries hydrologically connected to the lagoon, with results relevant to lagoon condition or contaminant inputs	Conducted outside the lagoon and its hydrologically connected drainage network, or without demonstrable relevance to the lagoon	E3
4	Thematic scope	Addresses water quality, environmental contaminants, or agricultural intensification and related pressure on the lagoon system	Does not address water quality, environmental contamination, or relevant agricultural pressure	E4
5	Environmental variables	Includes physicochemical or microbiological variables; metals; pesticides; pharmaceuticals; caffeine; plastics or microplastics; other emerging contaminants; or sedimentation/land-use indicators linked to agricultural pressure	Does not present relevant environmental variables or indicators of pressure on the lagoon system	E5
6	Full-text availability	Full text available for eligibility assessment	Full text unavailable	E6
7	Duplicates	Unique record	Duplicate record retrieved from more than one database	E7
8	Final eligibility	Meets all inclusion criteria, including direct study-area or hydrological relevance	Fails at least one inclusion criterion	E8

Table S3. Collection points for surface water samples in different locations of the Mirim Lagoon.

Points	Sites	South latitude	West longitude
P1	Rio Arroio Grande	32°15'20.66"	53° 04'53.19"
P2	Praia do Pontal	32°20'04.02"	52°49'18.39"
P3	Fazenda São Francisco	32°38'24.95"	53° 08'57.77"
P4	Capilha	32°29'20.70"	52°35'35.36"
P5	Vila Anselmi	32°54'32.80"	52°48'05.90"
P6	Porto Santa Vitória	33°29'48.05"	53°26′09″

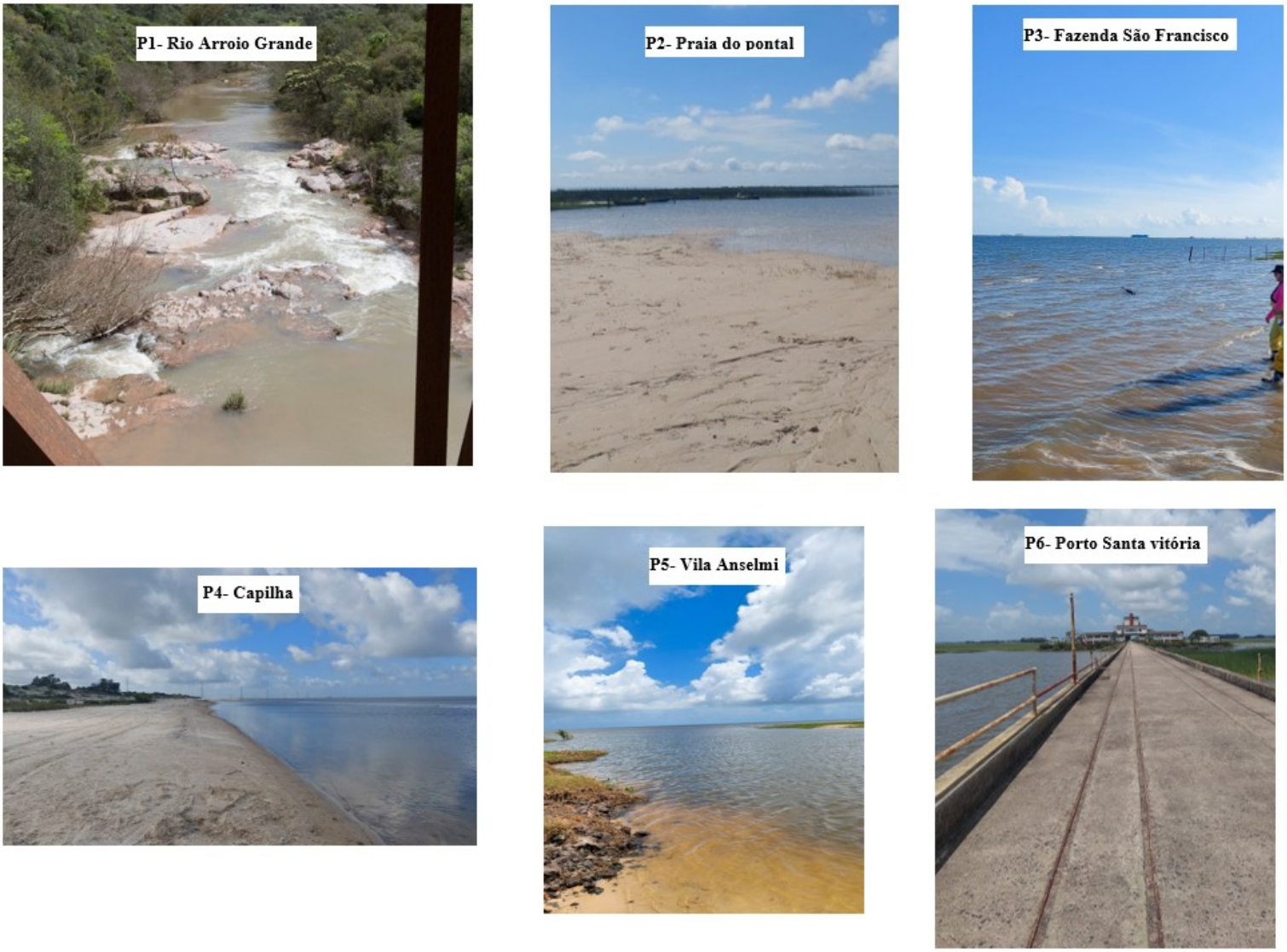


Fig. S2. Photographic records of the surface water sampling sites in Mirim Lagoon. Images correspond to the six sampling points evaluated in this study: P1, Rio Arroio Grande; P2, Praia do Pontal; P3, Fazenda São Francisco; P4, Capilha; P5, Vila Anselmi; and P6, Porto Santa Vitória.

Table S4. Physicochemical and microbiological parameters measured in surface water samples from the sampling sites in Mirim Lagoon across the four sampling times (T1–T4). Data were obtained from the monitoring database of the Agência de Desenvolvimento da Lagoa Mirim (ALM). NP = Not performed.

Periods	LOCAL	pH	Temperature	Conductivity	Salinity	Total phosphorus	Total nitrogen Kjeldal	Thermotolerant coliforms	Organic matter	Oxygen demand biochemical	Dissolved oxygen	Turbidity	Total solids	Chlorophyll *a*
	Points	-	ºC	uS/cm	ppm	mg P.L-1	mg N.L-1	NMP/100mL	mg O2.L-1	mg O2.L-1	mg O2.L-1	UNT	mg.L-1	µg/L
CONAMA Resolution No. 357/2005 (Class 2)	.	6,0 -9,0	≤ 40,0	.		≤ 0,03	.	≤1000		≤5	≥5,0	≤ 100	≤500	≤30
	P1	7.63	26.3	99.6	50.3	NP	NP	35000	2.62	1.13	6.27	14.4	116	NP
	P2	7.75	26.2	124.6	56.7	NP	NP	3.7	5.67	3.5	7.45	28.3	132	NP
T1	P3	7.89	29	74.3	37.6	NP	NP	49	6.98	2.68	7.09	34.5	129	NP
	P4	7.53	26.1	200	100	NP	NP	540	6.2	1.65	7.36	16.7	16.93	151
	P5	7.44	29.6	126	64	NP	NP	540	7.85	3.05	6.82	37.6	24.77	145.5
	P6	7.76	28.5	150	71	NP	NP	130	7.33	2.47	6.73	24.8	21.38	150.5
	P1	7.3	22.6	98.7	47.7	NP	NP	33	6.49	2.47	6.64	57.1	191	4.43
	P2	7.28	23.9	85.2	45.9	NP	NP	540	4.26	1.24	6.27	17.8	78	6.95
	P3	7.37	25.5	93.8	47.8	NP	NP	540	5.9	2.06	7.18	28.4	103	7.94
T2	P4	7.64	22.7	301	151	NP	NP	1600	7.19	0.99	7.27	19.9	184.5	NP
	P5	7.3	24.8	117.1	59	NP	NP	920	6.03	1.57	7.55	18.1	107	NP
	P6	7.9	25.9	122.2	61.3	NP	NP	280	7.19	3.3	8.64	31.9	130.5	NP
	P1	7.49	24	139.7	68.8	NP	NP	92000	3.47	2.16	6.36	26	144	0.66
	P2	7.49	25.5	119.3	57.1	NP	NP	6.8	4.21	1.65	7.18	16.6	102	8.91
T3	P3	8.14	28.9	131.5	64.2	NP	NP	49	4.57	1.65	8.09	22.5	106.5	4.74
	P4	7.78	25	221	111	NP	NP	27	5.82	2.45	8	25.2	149.5	16.24
	P5	7.52	21	420	210	NP	NP	540	8.06	1.45	6	39.3	275	10.22
	P6	7.89	21.8	124.3	62.5	NP	NP	22	5.56	1.55	7.36	26.6	114.5	NP
	P1	7.41	10.6	98.2	49.4	0.08	0	1100	2.23	1.31	9.71	24	105	0.8
	P2	7.54	11.5	205	103	0.04	0	4.5	5.05	2.35	10.58	28	186	13.9
T4	P3	7.86	11.9	168	83	0.04	0	17	8.18	1.4	10.1	42.9	154	4.54
	P4	7.86	11.2	258	131	0.03	0	ND	5.07	1.31	9.81	33	216.5	16.89
	P5	7.39	12.4	609	311	0.12	0	11	7.73	1.74	7.31	91.5	449.5	3.51
	P6	7.81	10.7	155.8	79.2	0.04	0	6.8	6.33	1.74	10.48	34.3	142.5	15.82

Table S5. Average values of total phosphorus and total nitrogen determined in surface water samples at different locations in Lagoa Mirim by the Lagoa Mirim Development Agency between 2017 and 2022. Source: Silva et al. (2024).

	Year	P1	P2	P3	P4	P5	P6
Total phosphorus	2017	3.19	8.99	8.82	13.10	12.88	6.11
	2018	0.26	0.35	0.38	0.41	0.44	0.40
	2019	0.28	1.13	1.30	2.10	1.60	1.99
	2020	2.27	3.56	6.11	6.03	4.17	3.06
	2021	4.05	6.85	8.51	6.56	5.47	5.55
	2022	4.06	3.83	2.34	5.75	4.68	4.29
total nitrogen	2017	7.63	5.94	4.88	5.59	4.48	6.80
	2018	3.44	2.56	3.70	4.47	7.68	4.86
	2019	2.03	4.34	6.09	5.42	4.21	5.56
	2020	1.07	4.67	2.16	1.72	0.41	1.87
	2021	1.07	2.39	3.05	0.65	0.81	0.84
	2022	6.57	1.40	1.05	1.01	1,65	1.21

Panel 1 of 3.

	DIA		2HA		DEA		atrazine		simazine		ametryn		caffeine		imidacloprid		hexazinone	
ng/L	média	desvpad	média	desvpad	média	desvpad	média	desvpad	média	desvpad	média	desvpad	média	desvpad	média	desvpad	média	desvpad
P4_jan	ND		8.4	0.0	5.2	0.1	5.0	0.0	ND		ND		234.8	25.3	7.9	1.5	ND	
P6_jan	6.7	0.1	22.4	0.2	11.4	0.3	13.4	0.4	1.3	0.0	ND		21.3	0.6	6.8	0.6	ND	
P8_jan	12.0	0.7	27.0	0.8	19.4	0.4	16.0	0.1	1.8	0.1	ND		55.2	2.2	7.9	0.5	ND	
P9_jan	10.7	0.6	9.9	0.0	16.5	0.2	11.4	0.0	ND		ND		79.4	3.3	4.6	0.2	ND	
P11_jan	9.7	0.2	12.1	0.3	16.8	0.0	23.7	0.2	1.3	0.0	ND		45.2	1.1	19.0	0.1	ND	
P12_jan	10.5	0.0	13.5	0.1	15.8	0.5	8.6	0.3	1.8	0.0	ND		40.4	5.1	5.2	0.3	ND	
P4_fev	3.2	0.3	2.7	0.1	5.4	0.1	6.2	0.0	1.3	0.0	ND		170.0	6.4	9.1	0.2	ND	
P6_fev	6.1	0.1	8.6	0.0	10.7	0.0	9.1	0.1	ND		ND		19.4	1.0	3.4	0.3	ND	
P8_fev	6.3	0.7	24.4	0.2	11.4	0.3	13.3	0.1	ND		ND		53.0	1.8	14.5	0.5	ND	
P9_fev	4.5	0.1	7.8	0.3	10.5	0.0	8.4	0.1	ND		ND		28.4	1.4	7.1	1.5	ND	
P11_fev	ND		18.2	4.2	16.4	1.6	ND		ND		ND		ND		ND		ND	
P12_fev	9.5	0.5	13.4	0.2	14.9	0.2	8.8	0.0	1.8	0.0	ND		35.1	0.9	5.5	0.2	ND	
P4_mar	4.9	0.5	4.8	0.1	7.3	0.1	6.0	0.1	1.7	0.1	ND		618.0	36.9	17.8	0.1	ND	
P6_mar	12.5	0.4	14.0	0.2	19.8	0.4	12.9	0.1	ND		ND		136.1	2.2	2.9	0.0	ND	
P8_mar	12.7	0.2	34.3	0.1	19.0	0.2	16.0	0.1	ND		ND		56.1	3.7	10.0	1.6	ND	
P9_mar	8.7	0.6	12.2	0.4	14.1	0.5	10.4	0.0	ND		ND		71.1	1.2	3.5	0.2	ND	
P11_mar	5.1	0.2	15.2	0.5	8.2	0.2	8.4	0.1	1.3	0.0	ND		27.4	1.6	7.7	0.3	ND	
P12_mar	9.2	0.9	10.2	0.3	12.3	0.5	8.9	0.2	3.5	0.1	ND		49.5	2.2	2.1	0.4	ND	
P4_jul	ND		ND		ND		3.6	0.0	ND		ND		329.5	1.9	1.0	0.2	ND	
P6_jul	6.5	0.3	8.9	0.4	10.2	0.3	9.2	0.1	ND		ND		315.2	3.0	7.7	0.5	ND	
P8_jul	2.5	0.3	11.6	0.1	6.0	0.1	8.1	0.1	ND		ND		77.5	2.4	180.5	2.7	ND	
P9_jul	8.2	0.8	9.1	0.3	13.3	0.3	10.5	0.3	ND		ND		30.8	4.3	2.0	0.2	ND	
P11_jul	4.2	1.3	8.2	0.5	6.7	0.2	7.3	0.2	1.4	0.1	ND		24.2	0.1	4.3	0.0	ND	
P12_jul	4.7	0.1	8.9	0.1	7.7	0.0	7.6	0.0	2.3	0.1	ND		20.4	0.2	ND		ND	

Fig. S3. Concentrations of emerging contaminants measured in surface water samples from Mirim Lagoon across the sampling periods. Values are expressed in ng/L as mean and standard deviation. ND indicates not detected. The complete dataset is presented in three landscape panels to improve readability. DIA, DEA e 2HA correspondem, respectivamente, aos metabólitos da atrazina desisopropilatrazina, desetilatrazina e 2-hidroxiatrazina.

Fig. S3. Continued. Panel 2 of 3.

	carbofuran		diuron		tebuconazole		epoxiconazole		propiconazole		profenofos		chlorpyrifos		carbendazim	
ng/L	média	desvpad	média	desvpad	média	desvpad	média	desvpad	média	desvpad	média	desvpad	média	desvpad	média	desvpad
P4_jan	1.4	0.0	16.4	1.3	5.3	0.1	ND		ND		ND		ND		2.1	0.1
P6_jan	ND		11.2	1.0	85.4	3.5	1.4	0.0	ND		ND		ND		3.9	0.0
P8_jan	ND		20.9	0.3	107.2	1.3	1.2	0.1	ND		ND		ND		4.0	0.0
P9_jan	ND		ND		17.0	0.3	ND		ND		ND		ND		1.4	0.0
P11_jan	ND		6.6	0.0	282.4	4.3	ND		ND		ND		ND		4.0	0.0
P12_jan	ND		ND		38.3	0.0	ND		ND		ND		ND		1.6	0.0
P4_fev	1.5	0.0	15.0	0.5	55.3	0.1	ND		ND		ND		ND		1.6	0.1
P6_fev	1.4	0.0	5.9	0.2	242.2	2.6	ND		ND		ND		ND		1.9	0.1
P8_fev	2.9	0.0	10.8	0.1	4999.4	47.1	ND		ND		ND		ND		2.8	0.0
P9_fev	ND		ND		21.4	1.3	ND		ND		ND		ND		1.3	0.0
P11_fev	ND		ND		425.6	20.4	ND		ND		ND		ND		ND	
P12_fev	1.6	0.0	ND		293.0	7.2	ND		1.5	0.2	ND		ND		1.5	0.0
P4_mar	9.0	0.1	4.6	1.1	50.5	1.2	ND		ND		ND		ND		3.4	0.0
P6_mar	ND		3.2	0.0	340.2	4.1	ND		ND		ND		ND		4.3	0.0
P8_mar	2.1	0.0	4.7	0.7	1217.6	2.7	12.9	0.2	ND		ND		ND		10.1	0.1
P9_mar	1.6	0.0	3.9	1.8	523.2	2.7	ND		ND		ND		ND		2.4	0.0
P11_mar	ND		5.1	1.2	1865.5	13.4	ND		ND		ND		ND		5.9	0.1
P12_mar	ND		ND		187.9	1.5	ND		ND		ND		ND		1.7	0.0
P4_jul	ND		ND		3.6	0.0	ND		ND		ND		ND		1.4	0.0
P6_jul	ND		8.1	0.0	84.8	1.0	ND		ND		ND		ND		2.2	0.0
P8_jul	ND		2.8	0.0	46.0	0.9	ND		ND		ND		ND		1.4	0.0
P9_jul	ND		ND		29.2	0.1	ND		0.4	0.1	ND		ND		1.6	0.0
P11_jul	ND		3.5	0.5	354.9	2.0	ND		ND		ND		ND		7.6	0.1
P12_jul	ND		ND		64.3	1.0	ND		ND		ND		ND		ND	

Fig. S3. Concentrations of emerging contaminants measured in surface water samples from Mirim Lagoon across the sampling periods. Values are expressed in ng/L as mean and standard deviation. ND indicates not detected. The complete dataset is presented in three landscape panels to improve readability. DIA, DEA e 2HA correspondem, respectivamente, aos metabólitos da atrazina desisopropilatrazina, desetilatrazina e 2-hidroxiatrazina.

Fig. S3. Continued. Panel 3 of 3.

	trimethoprim		thiamethoxam		tebuthiuron		azoxistrobin		malathion		metolachlor		trifloxistrobin		2,4-D		fipronil	
ng/L	média	desvpad	média	desvpad	média	desvpad	média	desvpad	média	desvpad	média	desvpad	média	desvpad	média	desvpad	média	desvpad
P4_jan	0.4	0.1	5.1	0.3	ND		2.7	0.2	4.2	0.1	19.8	1.5	ND		32.3	2.3	0.5	0.1
P6_jan	0.5	0.0	52.7	1.8	0.3	0.0	14.6	0.4	ND		40.3	0.8	ND		ND		0.6	0.0
P8_jan	1.5	0.0	48.9	2.7	0.4	0.0	21.1	0.6	ND		40.1	0.7	ND		13.0	1.0	0.6	0.1
P9_jan	ND		2.5	0.4	0.4	0.0	5.5	0.1	ND		8.6	0.0	ND		ND		ND	
P11_jan	ND		179.1	4.2	0.4	0.0	114.1	3.4	ND		17.6	0.5	ND		ND		1.0	0.1
P12_jan	ND		7.0	0.8	0.4	0.0	7.8	0.1	4.4	0.0	19.8	0.4	2.0	0.0	ND		ND	
P4_fev	0.4	0.0	2.6	0.0	ND		12.8	0.3	5.4	0.0	63.5	0.2	ND		628.4	12.7	1.8	0.1
P6_fev	0.3	0.0	16.8	0.1	0.3	0.0	42.2	0.6	ND		14.8	0.3	ND		ND		ND	
P8_fev	ND		32.3	0.2	0.3	0.0	20.7	0.0	ND		65.3	1.1	ND		10.9	0.7	0.4	0.1
P9_fev	0.6	0.1	ND		0.5	0.0	4.0	0.1	ND		7.4	0.2	ND		ND		ND	
P11_fev	ND		ND		ND		3.8	0.8	ND		ND		ND		ND		ND	
P12_fev	ND		18.0	0.5	0.4	0.0	75.4	0.4	ND		16.4	0.1	ND		ND		ND	
P4_mar	0.9	0.0	7.0	0.4	ND		8.8	0.2	5.3	0.0	13.7	0.0	ND		6.7	0.8	ND	
P6_mar	0.4	0.0	10.5	1.0	0.4	0.0	47.5	0.8	ND		7.7	0.0	ND		ND		ND	
P8_mar	2.2	0.0	17.7	0.6	0.3	0.0	62.1	0.2	ND		15.5	0.2	ND		ND		ND	
P9_mar	0.5	0.0	5.4	0.8	0.3	0.0	22.2	0.4	ND		8.1	0.3	ND		ND		ND	
P11_mar	0.6	0.0	7.3	0.8	0.4	0.0	30.8	0.6	8.1	0.1	4.6	0.1	ND		ND		0.3	0.1
P12_mar	ND		3.0	0.2	0.3	0.0	58.0	0.0	6.1	0.0	12.0	0.3	ND		ND		ND	
P4_jul	0.6	0.0	ND		ND		1.5	0.0	7.6	0.1	3.8	0.0	ND		4.0	0.0	ND	
P6_jul	ND		10.5	0.6	0.3	0.0	8.2	0.1	7.6	0.2	10.1	0.1	ND		51.3	0.1	0.3	0.1
P8_jul	0.6	0.0	11.6	0.9	0.3	0.0	6.2	0.1	4.8	0.0	17.4	0.6	ND		29.1	0.9	1.2	0.1
P9_jul	ND		2.8	0.4	0.4	0.0	11.3	0.1	5.8	0.1	9.8	0.1	ND		ND		ND	
P11_jul	0.8	0.0	ND		0.3	0.0	8.0	0.1	ND		6.1	0.0	ND		ND		0.7	0.1
P12_jul	ND		11.7	1.3	0.4	0.0	22.3	0.1	6.6	0.2	11.3	0.1	ND		26.3	1.4	ND	

CAPÍTULO 2

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Species-specific sensitivity to imidacloprid: ecotoxicological effects on congeneric cladoceran and ecological risk assessment

Abstract

Emerging contaminants are an increasing concern due to their widespread occurrence in different environmental matrices. Among them, pesticides frequently reach aquatic ecosystems and may cause adverse effects on aquatic biota. This study evaluated, under laboratory conditions, the effects of the neonicotinoid insecticide imidacloprid on congeneric cladoceran species commonly used in ecotoxicological studies, focusing on survival, reproduction, and feeding assay (ingestion rate). Acute toxicity tests were conducted with the exotic species *Daphnia similis* (1–5 mg/L), *D. magna* (4–64 mg/L), and *Ceriodaphnia dubia* (0.5–8 mg/L), as well as the native species *C. silvestrii* (0.5–8 mg/L). Chronic tests evaluated reproduction in *D. similis* and *D. magna* exposed to 0.025, 0.05, 0.1, and 0.2 mg/L. Feeding assays assessed ingestion rates in all four species exposed to 0.05, 0.1, and 0.2 mg/L. Additionally, species sensitivity distribution (SSD) curves were constructed, and environmental risks were estimated using the risk quotient (MEC/PNEC). The results revealed clear interspecific differences in sensitivity to imidacloprid, with decreasing acute toxicity in the order: *C. silvestrii* > *C. dubia* > *D. similis* > *D. magna*. Chronic exposure significantly reduced reproduction in both daphniid species, with effects observed from 0.025 mg/L. In feeding assays, *C. silvestrii* showed greater sensitivity, with reduced ingestion rates at 0.1 mg/L, whereas the other species did not exhibit significant changes. These findings highlight the importance of considering interspecific variability and including native species in environmental risk assessments of pesticides.

Keywords: *Ceriodaphnia silvestrii*; *Ceriodaphnia dubia*; *Daphnia magna*; *Daphnia similis*; Pesticide; Zooplankton

Introduction

Over the past decades, the occurrence of organic micropollutants derived from anthropogenic activities in aquatic environments has become increasingly evident. This trend is demonstrated by both the growing diversity of detected compounds and the concentration levels at which they are reported (Wilkinson et al. 2022). Many of these compounds, termed emerging contaminants, are not necessarily new; however, mainly due to limitations in analytical instrumentation in the past, they were previously undetectable. These include pharmaceuticals, personal care products, hormones, plasticizers, and pesticides (Reichert et al. 2019). Among emerging contaminants, pesticides stand out, particularly those characterized by high environmental persistence and high mobility, such as neonicotinoids, which since their introduction in the 1990s have become the most widely used insecticides worldwide, with records of use in more than 120 countries (Yang et al. 2025).

The insecticide imidacloprid, a widely used neonicotinoid, stands out due to its extensive commercialization and application (Agrofit 2025). It was the first neonicotinoid to be marketed in the 1990s in the United States and is currently one of the most widely used insecticides worldwide (Wang et al. 2025). It is applied as an insecticide for soil, seed, and foliar treatments in a wide range of crops, including cereals, cotton, fruits, potatoes, rice, sugarcane, maize, turf grass, and vegetables (Agrofit 2025). Its mode of action consists of causing insect mortality after ingestion or contact by affecting the nervous system through the blockage of postsynaptic acetylcholine receptors (Tomizawa et al. 2005). This systemic activity acts in a similar way in aquatic organisms, as it interferes with acetylcholine binding sites located in the extracellular domain of these receptors (Malhota et al. 2021).

Due to its chemical properties that increase environmental persistence and susceptibility to transport into aquatic ecosystems through runoff, imidacloprid is commonly detected at concentrations ranging from 0.001 µg/L (limit of detection > LOD) up to 320 µg/L - this concentration, detected in agricultural areas in the Netherlands (Van Dijk et al. 2013). In Brazilian ecosystems, reported concentrations range from 0.01 (Gonçalves et al. 2020) to 3.65 µg/L (Becker et al. 2009). In addition to its presence in aquatic ecosystems, this compound can cause adverse effects on non-target organisms belonging to different trophic levels, such as algae, zooplankton, and fish (Iturburu et al. 2017; Sumon et al. 2018). Especially for aquatic invertebrates, neonicotinoids can exert significant lethal and sublethal effects on populations, e.g., zooplanktonic cladocerans (Branchiopoda) (Morrissey et al. 2015). These sublethal effects include impaired reproduction and locomotion, stunted growth, and reduced foraging ability (Schöfer et al. 2023; Tison et al. 2020). These organisms constitute a crucial link in aquatic food webs, serving as prey for larger organisms such as fish and insects (Surendra e Bharti, 2015; Leite et al. 2022). When these organisms are affected due to their high sensitivity, they may trigger cascading effects and alter the performance of several other species within the trophic structure (Hayashi et al. 2020).

The genera *Daphnia* and *Ceriodaphnia* are the cladocerans most used in toxicological bioassays worldwide (El-Deeb Ghazy. 2011; ABNT NBR 12713 2016). These organisms feed by filtering algae and suspended particulate organic matter, thus contributing to the prevention of eutrophication and to improving water clarity in ponds and lakes. They show high sensitivity to environmental variations and aquatic contaminants, are easy to culture under laboratory conditions, reproduce by parthenogenesis (Buratini et al. 2004), and present a short life cycle and high reproductive consistency (Jeyavani et al. 2023). Three standardized and extensively used species in laboratory tests are *D. magna*, *D. similis*, and *C. dubia* (Domingues and Bertoletti 2008). *Ceriodaphnia dubia* is a microcrustacean measuring approximately 0.8 to 0.9 mm in length, with an oval-shaped body and 8 to 10 anal spines and is naturally found in Europe and North America (ABNT NBR 13373 2022). *Daphnia magna* is a microcrustacean exotic ranging from 2 to 6 mm in length and is distributed along the Northern Hemisphere. *Daphnia similis* is also an exotic

cladoceran in tropical aquatic ecosystems; it inhabits inland waters in temperate regions over the Northern Hemisphere, and reaches a maximum length of about 3.5 mm (Hudec 1991; Jeyavani et al. 2023; ABNT NBR 12713 2022).

In recent years, efforts have been made to use native tropical species in ecotoxicological assessments, particularly in Brazil, as they are more representative of the environments in which they occur and have often shown higher sensitivity to certain compounds when compared to congeneric species from temperate regions (Moreira et al. 2014; Mansano et al. 2018). One example is *Ceriodaphnia silvestrii*, a tropical species that can be found in South America, including the Brazilian states of São Paulo, Rio Grande do Sul, Goiás, and the Federal District, as well as in Argentina (Matsumura-Tundisi and Tundisi 2011). This species is considered easy to culture under laboratory conditions and, similarly to *C. dubia*, has a short life cycle (ABNT 2022) and high sensitivity to anthropogenic impacts, such as contamination by pesticides (Robles-Vargas 2015; Silva et al. 2020). In addition, this species shows rapid responses in chronic tests, which can be conducted in as little as eight days (Hayasaka et al. 2012), and it is extremely small (0.8–0.9 mm).

Although imidacloprid is widely used and regulated for agricultural purposes in Brazil, environmental criteria or reference values for this compound in surface waters are still nonexistent (CONAMA 2005). In contrast, regions such as the United Kingdom, the United States, and Canada have already established parameters for its evaluation in aquatic environments (European Commission, 2013; USEPA 2026; CCME 2007). This gap highlights the importance of long-term ecotoxicological studies in tropical conditions to support environmental risk assessment and the development of regulations. In view of the above, this study aimed to evaluate the acute and chronic toxicity of the insecticide imidacloprid in four cladoceran species, three exotic species (*D. similis*, *D. magna* and *C. dubia*) and one native species (*C. silvestrii*).

In acute tests with *D. magna*, *D. similis*, *C. dubia* and *C. silvestrii*, survival was assessed. In chronic tests, reproduction was evaluated only for the daphniids *D. magna* and *D. similis*. In the feeding assay (ingestion rate), in which the effects were compared among the four species (*C. silvestrii*, *C. dubia*, *D. similis*, and *D. magna*), food ingestion (microalgae) was evaluated. In addition, a sensitivity comparison among aquatic organisms was performed through the construction of species sensitivity distribution (SSD) curves, followed by an ecological risk assessment based on the risk quotient between the measured environmental concentration (MEC) and the predicted no-effect concentration (PNEC). We hypothesized that: (i) the relatively small-bodied native cladoceran *C. silvestrii* would be more sensitive to acute imidacloprid exposure than *D. magna*, *D. similis*, and *C. dubia*, exhibiting a lower 48-h immobilization EC_{50}; (ii) interspecific differences in feeding behavior, filtration rate, and physiological responses would result in greater inhibition of algal ingestion by *C. silvestrii*; and (iii) prolonged imidacloprid exposure would disrupt energy allocation to reproduction, reducing neonate production by *D. magna* and *D. similis* relative to their respective controls.

Materials and Methods

Culture and maintenance of test organisms

All culturing procedures and experiments with the cladocerans *D. similis* and *D. magna* followed the recommendations of the *Daphnia* spp. test method described in the standard protocol ABNT NBR 12713 (2022). For the cladocerans *C. silvestrii* and *C. dubia*, the test method for *Ceriodaphnia* spp. established by ABNT NBR 13373 (2022) was followed.

Individuals of *Daphnia* spp. were maintained in 2 L glass beakers containing 1.5 L of natural water, while *Ceriodaphnia* spp. were maintained in 600 mL glass beakers containing 500 mL of reconstituted medium (MS). The culture media were completely renewed twice a week. Both species were fed with the microalga *Raphidocelis subcapitata*, with 10^5 cells mL^{-1} for *Ceriodaphnia* spp. and 10^6 cells mL^{-1} for *Daphnia* spp. and a mixed organic supplement composed of biological yeast and fish feed. *Daphnia* spp.

cultures were maintained under a photoperiod of 16 h light: 8 h dark at 20 ± 2 °C, while *Ceriodaphnia* spp. cultures were maintained under a photoperiod of 12 h light and 12 h dark at 25 ± 2 °C.

Insecticide and chemical analysis

The pesticide used in this study was the commercial insecticide Imidagold 700 WG® (700 g kg^{-1} of active ingredient). For use in the ecotoxicological assays, a stock solution at a nominal concentration of 100 mg L^{-1} (expressed as active ingredient) was prepared by dissolving the commercial formulation in ultrapure water. The solution was stored under refrigeration at 4 °C and protected from light until preparation of the test dilutions. From this stock solution, the experimental concentrations used in each assay were obtained by serial dilution as described below.

To confirm the nominal concentrations of the insecticide imidacloprid used in the tests, the test solutions were analyzed by liquid chromatography coupled to triple quadrupole mass spectrometry (LC–MS/MS) (Agilent Technologies, model 1200, 6410). The quantification of the analyte imidacloprid was performed by direct injection, without the need for an extraction step. The samples were filtered through a hydrophilic polytetrafluoroethylene (PTFE) syringe filter (13 mm diameter, 0.22 µm pore size) (Analítica, São Paulo, Brazil). After filtration, 750 µL of each sample was transferred to a vial containing 50 µL of H_2O:MeOH solution (70:30, v/v) with the internal standard imidacloprid-d4 at a concentration of 50 µg L^{-1}, resulting in a 1.07-fold dilution factor. Instrumental analysis was then performed.

The analyte was determined using a Thermo Vanquish liquid chromatograph coupled to a Thermo Fortis triple quadrupole mass spectrometer with electrospray ionization (ESI). Chromatographic separation was performed on a Zorbax SB-C18 column (2.1 × 30 mm, 3.5 µm particle size). The analyte was determined using selected reaction monitoring (SRM) with positive ionization mode. The calibration curve was constructed over a concentration range of 1 to 500 µg/L, with an instrumental limit of quantification (iLOQ) of 5 µg/L and a method limit of quantification (LOQ) of 5 µg/L.

Acute toxicity test

Five Daphnids organisms (neonates less than 24 hours old, obtained from females aged between 12 and 25 days) and five *Ceriodaphnia* spp. organisms (neonates less than 24 hours old, obtained from females aged between 5 and 18 days) were distributed into four test containers containing increasing concentrations of the insecticide. For *C. silvestrii* and *C. dubia*, the concentrations tested were 0,5, 1, 2, 4, and 8 mg/L (of active ingredient), plus a control treatment, in a final volume of 10 mL of test solution. For *D. similis*, the concentrations used were 1, 2, 3, 4, and 5 mg/L (of active ingredient), and for *D. magna*, 4, 8, 16, 32, and 64 mg/L (of active ingredient) were applied, both in a final volume of 15 mL of test solution. The concentration ranges differed between the species (*D. magna* and *D. similis*) because preliminary range-finding tests indicated distinct sensitivities to imidacloprid. The species *D. similis* was more sensitive, whereas *D. magna* required higher concentrations to obtain an adequate concentration-response curve and to estimate the EC_{50}.

The exposure was conducted in incubator chambers for 48 h, without feeding and without renewal of the test solutions. During this period, pH, temperature, dissolved oxygen, and electrical conductivity were measured in all samples at the beginning and at the end of the test. After 48 h, the number of immobile organisms was recorded. Subsequently, the EC_{50} (median effective concentration) values were calculated using RStudio software version 4.4.1 (Posit Software, PBC; version 2024.04.1+748).

Species sensitivity distribution (SSD)

The toxicity data used to construct the species sensitivity distribution (SSD) curves were obtained from the mean EC_{50}–48 h values determined in this study for the four cladoceran species tested (*D. magna*, *D. similis*, *C. dubia*, and *C. silvestrii*), based on three independent acute tests with a duration of 48 h conducted for each species. In addition, acute EC_{50}–48 h values for other aquatic organisms were obtained from the literature, including the study by Suzuki et al. (2024) and the data presented in Table 3 of the report *"Water Quality Criteria Report for Imidacloprid"* (Bower e Tjeerdema 2019).

The SSD was constructed using R software (version 4.4.1). Initially, EC_{50} values were converted to the $\log_{10}$ scale, since ecotoxicological data typically follow a log-normal distribution, which is a fundamental assumption for the statistical modeling of this type of curve (Aldenberg e Jaworska 2000). Subsequently, the cumulative distribution of toxicity values was fitted to a log-normal model by calculating the mean and standard deviation of the log-transformed values. Based on this fit, a cumulative distribution curve was generated, representing the proportion of species potentially affected as a function of the insecticide concentration.

The hazardous concentration for 5% of the species (HC_5) was estimated directly from the 5th percentile of the fitted log-normal distribution, representing the concentration at which 95% of the species in the community are expected to be protected. To quantify the uncertainty associated with the HC_5 estimate, a bootstrap resampling procedure (n = 10,000) was applied, in which EC_{50} values were resampled with replacement to calculate 95% confidence intervals. The final HC_5 values and their respective confidence intervals were then used in the acute ecological risk assessment, allowing the comparison of reported environmental concentrations with concentrations associated with potential adverse effects on the aquatic community.

Ecological Risk Assessment

The acute ecological risk assessment of the insecticide imidacloprid was conducted based on the results of the species sensitivity distribution (SSD) curve. Risk was characterized using the risk quotient (RQ), calculated directly as the ratio between the measured environmental concentration (MEC) and the HC_5 value derived from the SSD, according to the following equation:

$$QR = \frac{MEC}{HC_5}$$

where MEC represents the environmental concentration reported in Brazilian surface waters, and HC_5 corresponds to the concentration predicted to affect 5% of the most sensitive aquatic species in the community.

For this assessment, environmental concentrations of imidacloprid from 11 studies reported in the scientific literature for Brazilian ecosystems (28 Brazilian freshwater bodies) were considered, ranging from 0.01 to 3.65 µg L^{-1} (Acayaba et al. 2021; Becker et al. 2009). The RQ values were interpreted according to the classification proposed by Sánchez-Bayo et al. (2002):

- RQ < 0.01 = negligible risk
- 0.01 ≤ RQ < 0.1 = low risk
- 0.1 ≤ RQ < 1 = moderate risk
- RQ ≥ 1 = high risk

Feeding assay (ingestion rate) with *Ceriodaphnia* spp. and *Daphnia* spp.

Feeding tests were conducted following the experimental procedure described by Silva et al. (2015). Initially, test neonates (< 24 h old) were separated from the culture medium and transferred to 1 L flasks under the same culture conditions, without feeding until the start of the experiments. The organisms remained fasting until they reached the age required for the assays: 96 h for *D. similis* and *D. magna*, and 48 h for *C. silvestrii* and *C. dubia*.

The experiments were performed in flasks containing 100 mL (*Daphnia* spp.) or 20 mL (*Ceriodaphnia* spp.) of the test solution, with five organisms per flask. The test solutions consisted of an initial concentration of 5×10^5 cells/mL of *Raphidocelis subcapitata*, to which imidacloprid was added directly at concentrations of 0.05, 0.1, and 0.2 mg/L. There was no pre-exposure of the algae to the insecticide. Five replicates were used for each treatment with five organisms inside, including: (i) control (algae + organisms, no insecticide), (ii) treatments (algae + organisms + insecticide), and (iii) blank (algae only, no organisms and no insecticide), to monitor algal growth. The assays were conducted at 20 ± 2 °C for *Daphnia* species and 25 ± 2 °C for *Ceriodaphnia* species, in the absence of photoperiod, to prevent algal growth during the 24 h exposure period. After 24 h of exposure, the test solutions were fixed with borate-buffered formalin, flash-frozen in liquid nitrogen, and stored at −20 °C until cell density analysis. pH, temperature, dissolved oxygen, and electrical conductivity measurements were performed at the beginning and end of the 24 h exposure period.

Samples were analyzed using a flow cytometer (FACSCalibur, Becton Dickinson, San Jose, CA, USA) equipped with a 15-mW blue argon-ion laser (488 nm excitation), using an internal standard (6 µm fluorescent beads; Fluoresbrite® carboxylate microspheres, Polysciences, Warrington, PA, USA). Cell density was determined by analyzing the FL3-H (red fluorescence) versus SSC-H (side scatter) channels, following the procedures described by Sarmento et al. (2008). Cytometric data were processed using FlowJo software (version 10.0; Tree Star Inc., USA). Algal ingestion rates were estimated from the temporal variation in cell density, following the method proposed by Villarroel et al. (1999). Although the original approach includes the calculation of filtration rate as an intermediate step, in this study only ingestion rates were considered for analysis. Ingestion was calculated based on the geometric mean concentration of algae throughout the experiment, normalized by the number of organisms and the exposure time. The ingestion rates (I; cells ind^{-1} h^{-1}) were calculated as:

$$I = \frac{V}{n} \times \frac{\ln C_0 - \ln C_t}{t} \cdot \sqrt{C_0 \times C_t}$$

Where I corresponds to the ingestion rates (cells ind^{-1} h^{-1}); C_0 and C_t are, respectively, the initial (0 h) and final (24 h) algal densities (cells mL^{-1}); N is the number of organisms per replicate in a test solution with a volume V (mL); T is the exposure time; and $\sqrt{(C_0 \times C_t)}$ represents the actual mean algal concentration to which the organisms were exposed during the experimental period.

Chronic toxicity test with daphnids

Neonates (6–24 h old) were also subjected to exposure to imidacloprid in chronic assays, which lasted up to 15 days for the species *D. similis* and 21 days for *D. magna*, in accordance with OECD Test Guideline 211 (OECD, 2012). Based on the environmental concentrations of imidacloprid described in the introduction, the concentrations of 0.025, 0.05, 0.1, and 0.2 mg/L

were selected for the study. Ten replicates containing 50 mL of test solution were prepared for each concentration, including the control, with one organism in each replicate. Every 48 hours, the test solutions were renewed, and the adult individuals were fed with microalgae (*Raphidocelis subcapitata*) and biological yeast. The neonates produced during this period were also counted and removed. Environmental conditions were maintained at 20 °C, with a photoperiod of 16 h of light and 8 h of darkness. Additionally, measurements of pH, temperature, dissolved oxygen, and electrical conductivity were performed in all samples from the beginning to the end of the test. Tests with the other species *C. silvestrii* and *C. dubia* were carried out, but they were not validated according to the validation criteria of ABNT NBR 13373 for the assessment of chronic toxicity in *Ceriodaphnia* spp. (ABNT 2022).

Endpoint	*D. similis* 	*D. magna* 	*C. dubia* 	*C. silvestrii* 
Acute tests (48h) n= 20 4 reps × 5 orgs) + control	1, 2, 3, 4, 5 mg/L	4, 8, 16, 32, 64 mg/L	0.5, 1, 2, 4, 8 mg/L	0.5, 1, 2, 4, 8 mg/L
Feeding assay (24 h) n= 25 5 reps × 5 orgs) + blank + control	0.05, 0.1, 0.2 mg/L	0.05, 0.1, 0.2 mg/L	0.05, 0.1, 0.2 mg/L	0.05, 0.1, 0.2 mg/L
Reproduction (15-21 d) n= 10 10 reps x 1 orgs + control	0.025, 0.05, 0.1, 0.2 mg/L	0.025, 0.05, 0.1, 0.2 mg/L	Not tested	Not tested

Fig. 1 Experimental design of laboratory trials evaluating the effects of imidacloprid on four cladoceran species (*D. similis*, *D. magna*, *C. dubia*, and *C. silvestrii*). Acute tests (48h) to assess immobility, feeding assay (24 h) to assess algae ingestion rates, and chronic reproduction tests (15–21 days) evaluating the number of neonates produced per female. Chronic tests with the other species, *C. silvestrii* and *C. dubia*, were conducted but were not validated according to the validation criteria of the ABNT NBR 13373 standard for the assessment of chronic toxicity in *Ceriodaphnia* spp. (ABNT, 2022).

Data analysis

EC_{50} values from the acute toxicity tests were calculated using three-parameter logistic curves. The significance level was set at 95% ($p < 0.05$) and was evaluated by one-way analysis of variance (ANOVA), followed by Tukey's test when the data met the assumptions of normality and homoscedasticity, verified using the Shapiro–Wilk test. For data that did not meet the normality assumption, the non-parametric Kruskal–Wallis test was applied, followed by Dunn's post hoc test to identify significant differences between the analyzed concentrations and the control groups. All analyses (acute, chronic, ingestion, SSD, and ecological risk assessment) were performed using RStudio software version 4.4.1 (Posit Software, PBC; version 2024.04.1+748).

Results

Chemical analysis

The imidacloprid concentrations in the solutions used in the chronic assay and feeding assay were quantified at the beginning of the experiment, in order to characterize the concentrations actually present in the exposure samples. The nominal concentrations prepared were 0.025, 0.05, 0.1, and 0.2 mg/L, while the average quantified concentrations were 0.013 ± 1.80, 0.03 ± 8.45, 0.05 ± 0.74, and 0.143 ± 33.19 mg/L, respectively.

Acute toxicity tests

During the acute toxicity tests, the mean pH values in the treatments ranged from 6.41 to 7.52. The water temperature measured in the treatments ranged between 19 and 20 °C for daphnids and between 24 and 25 °C for *Ceriodaphnia*, and the dissolved oxygen content measured in the test solutions ranged from 5.4 to 7 mg/L. In addition, the percentage of immobile organisms in the control was less than or equal to 10% at the end of the test. It means that the toxicity assays met the validity criteria specified in the guidelines for the test methods with *Ceriodaphnia* spp. (ABNT NBR 13373 (2022) and *Daphnia* spp. (ABNT NBR 12713 (2022).

The EC_{50} (48 h) values for the four species exposed to the commercial insecticide Imidacloprid 700 WG were estimated separately for each organism based on three acute toxicity tests. For *D. magna*, the EC_{50} was 30.85 ± 3.63 mg/L; for *D. similis*, it was 2.35 ± 1.34 mg/L; for *C. dubia*, the EC_{50} was 1.64 ± 0.48 mg/L; and for *C. silvestrii*, it was 1.50 ± 0.11 mg/L. According to the results, the sensitivity of the species to the insecticide imidacloprid followed the order: *C. silvestrii* > *C. dubia* > *D. similis* > *D. magna*. *C. silvestrii, C. dubia*, and *D. similis* were the species that showed the greatest sensitivity to the insecticide imidacloprid compared to *D. magna*, which presented an EC_{50} (48 h) value up to twenty times higher than that of the other species, being substantially less sensitive to the tested compound.

Species Sensitivity Distribution (SSD) and Ecological Risk Assessment

According to the constructed species sensitivity distribution curve (Fig 2), the most sensitive species was the ostracod *Cypridopsis vidua* (3.0 µg/L), followed by other sensitive taxa such as the cyclopoid *Tropocyclops* sp. and the ostracod *Cyprietta seuratti*, whereas *D. magna* showed the lowest sensitivity, based on the acute test values (48 h) (Table S1). The acute SSD (EC_{50} –48 h; 14 species) indicated an HC_5 of 6.57 µg/L, with lower and upper limits of 1.18 µg/L and 76.49 µg/L (95% CI: 1.18–76.49 µg/L), respectively. The HC_5 value represents the concentration that would protect 95% of the species; environmental concentrations above the HC_5 indicate a high probability of effects on ≥ 5% of the species and a risk of changes in community composition.

The measured environmental concentrations (MECs) used in the ecological risk assessment were obtained from literature data available for Brazilian freshwater systems. The minimum and maximum values reported for different water bodies and agricultural regions were used. These values were applied to represent the most sensitive scenario (worst case) and the most tolerant scenario (best case) in the estimation of ecological risk quotients (Table S2). The HC_5 values and their lower and upper limits, MEC (minimum/maximum), and RQ (minimum/maximum) for imidacloprid are shown in Table 1.

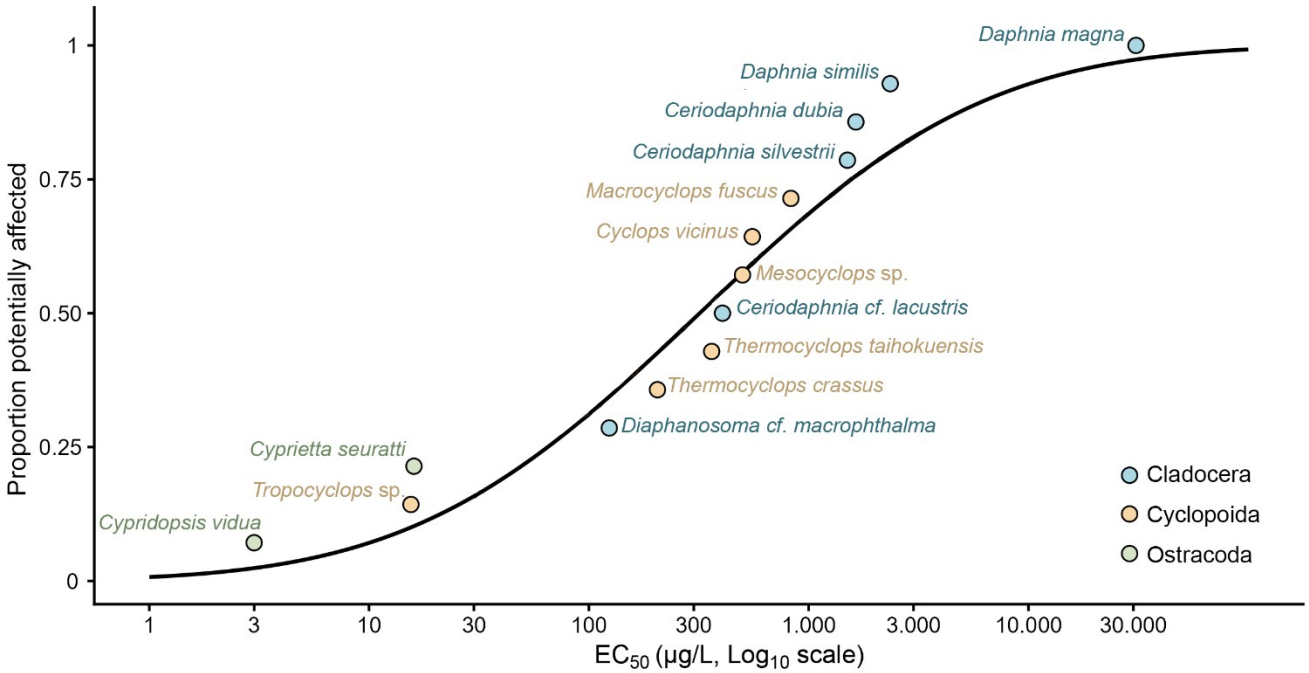


Fig. 2 Species sensitivity distribution (SSD) curve comparing the sensitivity to imidacloprid of the cladocerans tested in the present study, other cladocerans, copepods, and ostracods from the studies of Suzuki et al. (2024) and Bower and Tjeerdema (2019).

Table 1 Environmental risk of imidacloprid expressed as the ecological risk quotient (RQ), based on the hazardous concentration for up to 5% of the species in the SSD (HC_5—µg/L), with lower and upper limits of 1.18 µg/L and 76.49 µg/L, respectively.

Scenario HC_5	HC_5 (µg/L)	MEC minimum (µg/L)	RQ minimum (µg/L)	MEC maximum (µg/L)	RQ maximum (µg/L)
Central	6.57	0.01	0.0015	3.65	0.556
IC95% (lower)	1.18	0.01	0.0085	3.65	3.09
IC95% (upper)	76.49	0.01	0.00013	3.65	0.0477

The RQ values, calculated from the measured environmental concentration (MEC) and the HC_5 derived from the sensitivity curve based on acute toxicity data, ranged from 0.0015 to 0.556 in the central scenario, indicating negligible to moderate risk for aquatic species. The value of 1.18 µg/L represents the most sensitive scenario (worst case), whereas 76.49 µg/L represents the most tolerant scenario (best case). In the lower 95% confidence interval scenario (95% CI lower), the RQ values ranged from 0.0085 to 3.09, indicating high ecological risk. The RQ value of 3.09 deserves particular attention, as it reflects the combination of the highest measured environmental concentration and the lower limit of the HC_5 confidence interval; thus, an RQ > 1 indicates high ecological risk under this most sensitive scenario. In the upper 95% confidence interval scenario (95% CI upper), the RQ values ranged from 0.00013 to 0.0477, indicating low risk for the Brazilian freshwater biota, even at the maximum reported environmental concentration.

Feeding assay (ingestion rate) with *Ceriodaphnia* spp. and *Daphnia* spp.

After 24 hours of exposure to the insecticide, it was observed that, in the experiment with *C. silvestrii*, the concentration of 0.1 mg/L inhibited the algae's ingestion rates compared to the control ($p < 0.05$) (Fig 3B). For the other species, none of the treatments differed statistically from the control ($p > 0.05$), indicating that imidacloprid did not significantly affect the ingestion rates of *D. similis*, *D. magna*, and *C. dubia* (Figures 3A, 3C, and 3D).

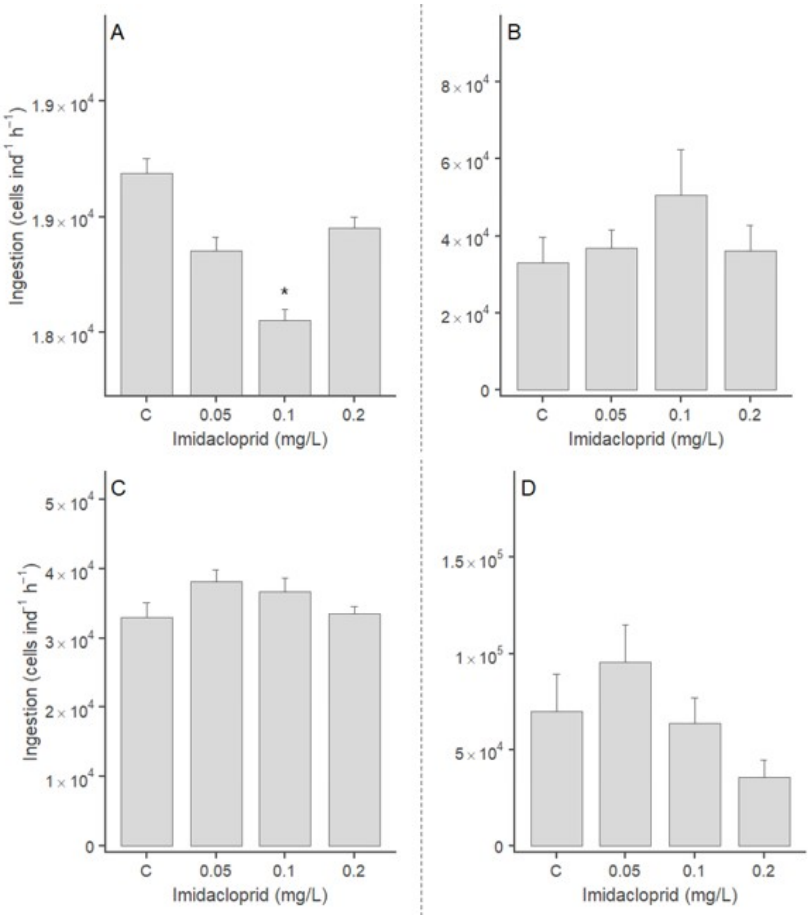


Fig. 3 Algal ingestion rates by *C. silvestrii* (A), *C. dubia* (B), *D. similis* (C) e *D. magna* (D) after 24 h of exposure to Imidagold 700 WG. Bars represent the mean ± standard error (n = 5), and the "*" indicates a statistically significant difference between the concentrations and the control (Dunn's test, $p < 0.05$).

Chronic toxicity test

In the present study, the chronic toxicity of imidacloprid was evaluated for the daphnids *D. magna* and *D. similis*. Female mortality of *D. similis* and *D. magna* did not exceed 20%, and the mean number of live offspring produced by animals at the end of the test was > 60% in the control, being accordingly to the validation criteria of the OECD/211 test (2012). After 15 days of exposure to sublethal doses of imidacloprid, a significant inhibition in the total number of neonates produced by *D. similis* females was observed (Fig 4A). The concentrations that caused statistically significant differences in reproduction

for *D. similis* were 0.025, 0.1, and 0.2 mg/L (Dunn's test, $p < 0.05$), and the EC_{10}, EC_{20}, and EC_{50} based on the reproduction inhibition were calculated as 0.0001 ± 0.0003 mg/L, 0.001 ± 0.003 mg/L, and 0.27 ± 0.20 mg/L, respectively.

After 21 days of exposure to sublethal doses of imidacloprid, there was also a significant decrease in the total number of neonates produced by *D. magna* females. In this case, all treatments differed significantly from the control, namely 0.025, 0.05, 0.1, and 0.2 mg/L (Dunn's test, $p < 0.05$) (Fig 4B). However, the attempt to estimate EC_{10}, EC_{20}, and EC_{50} was not feasible because data did not allow an adequate fit of the mathematical model.

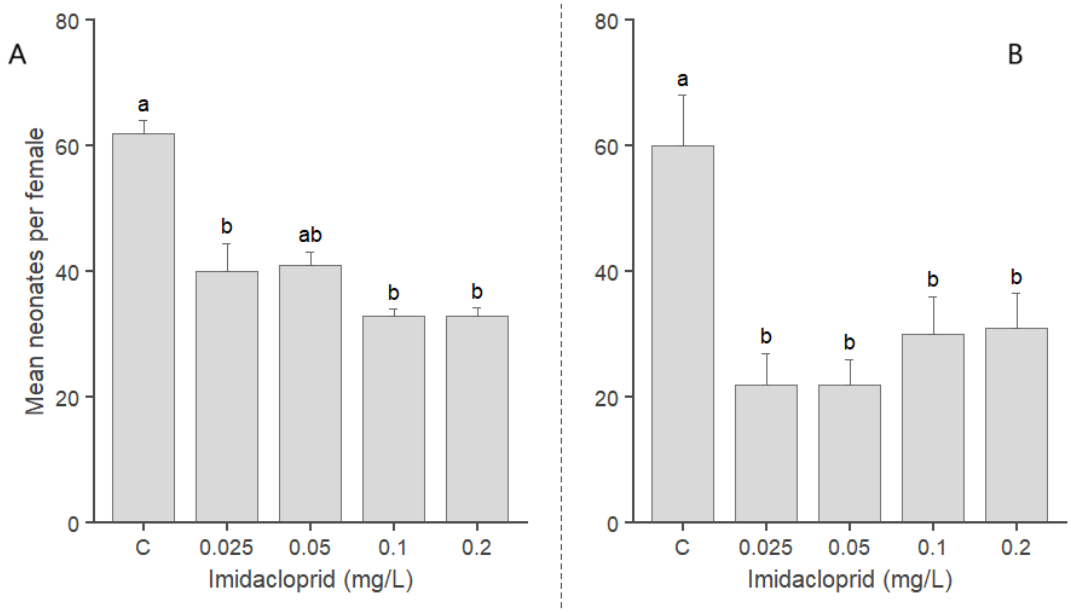


Fig. 4 Effects on the reproduction of *D. similis* exposed for 15 days to Imidagold 700 WG (A) and *D. magna* exposed for 21 days to Imidagold 700 WG (B). Bars represent the mean ± standard error (n = 10), and different letters indicate statistically significant differences (Dunn's test, $p < 0.05$).

Discussion

Acute toxicity tests and species sensitivity

Interspecific variation in sensitivity to the insecticide imidacloprid was observed among the studied species. As shown in the species sensitivity distribution curve (Fig 2), ostracods exhibited the highest sensitivity, cyclopoid copepods showed intermediate sensitivity, and cladocerans, *C. silvestrii*, *C. dubia*, *D. similis*, and *D. magna*, the species tested in the present study, were more tolerant to the insecticide. Based on the EC_{50} values obtained in this study, *D. magna* is 10 to 20 times more tolerant to imidacloprid than the other species. This species has been reported as the least sensitive to neonicotinoids, with effects observed only at concentrations > 40 mg/L (Raby et al. 2018). Li et al. (2020) also tested the acute toxicity of imidacloprid and found that *D. magna* was highly tolerant to short-term single exposure to imidacloprid (96 h EC_{50} of 8.47 µg/mL). Toxicokinetic and toxicodynamic processes are related to the factors that influence this interspecific variation. The rate of uptake and transport of the compound to the nAChR structure (the common site of action of neonicotinoid insecticides), as well as the metabolic capacity for biotransformation or detoxification of the pesticide, can significantly influence the expression of the observed toxic effects (Rico and Van den Brink, 2015). For example, the rapid clearance of imidacloprid from the tissues of *D. magna* may explain its greater

tolerance to the compound. Although about 84% of imidacloprid is initially distributed to soft tissues, the insecticide is rapidly eliminated ($t_1/_2$ = 1.2 h), preventing internal accumulation. This efficient elimination prevents the pesticide from reaching lethal concentrations within the body, which may explain why this species shows greater tolerance (higher EC_{50}), minimizing acute toxic effects (Li et al. 2020).

The study by Chen and Kuo (2018) presents a kinetic bioconcentration factor (BCF) model for amphipods, applicable to non-ionic compounds as well as to polar and ionizable compounds, such as imidacloprid. The model was based on uptake and elimination processes, parameters that are also commonly used to interpret tolerance in microcrustaceans. The authors concluded that the elimination of these compounds may be related to chemical interactions with the exoskeleton, which is composed of chitin (a carbohydrate), proteins, and calcium carbonate (bioash), increasing the retention of polar substances in amphipods and other crustaceans. This mechanism could explain the higher sensitivity observed in these organisms, which have an additional sorption capacity for such compounds, possibly through both the exoskeleton and the lipid membrane, allowing polar compounds to be retained for longer periods. Thus, the authors suggest that future studies should further investigate these mechanisms in greater detail.

Some authors suggest a relationship between body size and sensitivity, that is, insecticides affect smaller cladoceran species more strongly than larger ones (Hanazato 1998). For example, Hayasaka et al. (2012), when evaluating differences in the susceptibility of five cladoceran species to imidacloprid and fipronil, observed a positive relationship between the body length of each species and the acute toxicity (EC_{50}) of the insecticides. *C. dubia* was about 100 times more sensitive than the other species. For imidacloprid, toxicity decreased in the following order:
C. dubia > *C. reticulata* > *D. pulex* > *D. magna* > *M. macrocopa*. For fipronil, the order was:
C. dubia > *C. reticulata* > *M. macrocopa* > *D. pulex* > *D. magna*. Hayasaka et al. (2013) found EC_{50} (48 h) values for *C. dubia* similar to those obtained in this study (0.57 mg/L) for imidacloprid, and an EC_{50} of 1.69 mg/L for clothianidin (another neonicotinoid insecticide tested). Based on the EC_{50} (48 h) values from the acute tests of the present study, *D. magna*, the species with the largest body size (ranging from 2 to 6 mm in length), also showed greater tolerance to imidacloprid, possibly due to its larger body volume, which favors internal dilution of the contaminant and prevents its accumulation. In contrast, *C. silvestrii* and *C. dubia*, smaller species (ranging from 0.8 to 0.9 mm in length), exhibited higher sensitivity.

Finally, sensitivity may vary between native and exotic species. For example, in a comparative study of the acute toxicity of the herbicide atrazine to cladocerans, the EC_{50} (48 h) for *C. silvestrii* was 12.37 ± 2.67 mg/L and for *M. flabelligera* was 14.30 ± 1.55 mg/L, both being more sensitive to the compound than *D. magna*, which presented an EC_{50} (48 h) of 50.41 ± 2.64 mg/L (Moreira et al. 2014). The study by Mansano et al. (2018) also showed that both acute and chronic toxicity indicate that *C. silvestrii* is among the most sensitive invertebrate species to both tested compounds, including the active ingredients diuron and carbofuran as well as their commercial formulations, Diuron Nortox® 500 SC and Furadan® 350 SC. Moreira et al. (2020) compared interspecific sensitivity and found that *C. silvestrii* was the third most sensitive cladoceran among all evaluated microcrustaceans, including *D. magna* and *C. dubia*, in response to exposure to fipronil. When comparing the sensitivity of temperate and tropical freshwater cladocerans to the insecticide chlorpyrifos, Raymundo et al. (2019) found that the order of sensitivity among cladocerans was: *C. silvestrii* (0.039 µg L^{-1}) > *Diaphanosoma birgei* (0.211 µg/L) = *D. laevis* (0.216 µg/L) > *Moina micrura* (0.463 µg/L) = *Macrothrix flabelligera* (0.619 µg/L). In the SSD comparing sensitivity to chlorpyrifos, *C. silvestrii* was ten times more sensitive than the standard temperate test species such as *D. magna* (Raymundo 2019). In addition, several other studies emphasize the higher sensitivity of native species to pesticides and other contaminants (Alexandre et al. 2025; Valença et al. 2024; Daam and Van den Brink 2010; Gazonato Neto et al. 2019; Freitas and Rocha 2011). These findings reinforce the importance of using native tropical species in ecotoxicological studies in order to adequately assess and quantify local ecological impacts (Rocha et al. 2025).

Based on the results of this study, along with the literature, native tropical species, such as *C. silvestrii*, present greater sensitivity when compared to standard test species, such as *D. magna*. However, this response may vary depending on the species included in the sensitivity distribution. Therefore, species selection is an important factor in accurately representing ecological risk and deriving water quality criteria.

Species Sensitivity Distribution (SSD) and Ecological Risk Assessment

The taxon Ostracoda was the most sensitive taxonomic group to imidacloprid in the constructed SSD. The same result was observed in the study by Daam et al. (2013), who evaluated the aquatic risk of imidacloprid applied in an experimental rice field when the species *D. magna*, the ostracod *Heterocypris incongruens*, the alga *Pseudokirchneriella subcapitata*, and the aquatic plant *Lemna minor* were exposed. *H. incongruens* was the species that proved to be the most sensitive to imidacloprid, with a 6-day growth inhibition EC50 between 0.01 and 0.015 mg/L (10 to 15 µg/L) – levels lower than those for *D. magna* – 48 h-EC50 – 84 mg/L. Another study conducted in experimental rice fields for the assessment of ecological effects observed the absence of *Chironomus yoshimatsui* and of rice-field typical ostracods (Ostracoda: Cyprididae) after the introduction of the insecticide imidacloprid. In fields treated with imidacloprid, communities showed significantly lower abundances of organisms, and the most visible effects occurred when imidacloprid residues in the water were above ~ 1 µg/L (Sanchez-Bayo and Goka 2006). In general, the application of insecticides shows a slow recovery of ostracods (Sánchez-Bayo and Goka 2011) or a rapid decline in population size (Sánchez-Bayo, 2006). Casado-Martínez et al. (2019) also observed that, using standardized contact and growth bioassays with ostracods, dipteran nymphs, and nematodes, ostracods (*H. incongruens*) were the most sensitive to sediment contamination by pesticides, mainly chlorpyrifos and cypermethrin.

Copepods, the second most sensitive group, also proved to be sensitive to other agrochemicals. Leboulanger et al. (2011) compared the toxicity of two herbicides (diuron and paraquat) and two insecticides (temephos and fenitrothion) on nauplii of two strains of copepods of the genus *Mesocyclops* - one of tropical origin (*Mesocyclops aspericornis*) and the other of temperate origin. *Mesocyclops* from the temperate strain was more sensitive, for which it was possible to estimate an EC_{50} for paraquat of 152 µg/L and, for the insecticides temephos and fenitrothion, EC50 values of 45 µg/L and 1.017 µg/L. For *M. aspericornis* (tropical), EC_{50} values were 207 µg/L, 1450 µg/L, and 1.840 µg/L, demonstrating that two populations, even within the same genus, respond differently. In the study by Suzuki et al. (2024), the LC_{50} of most cyclopoid copepod species was lower than the concentrations of imidacloprid reported in rice fields (∼ 49 µg/L). When compared with cladocerans, the difference in sensitivity cannot be explained by life stage, collection conditions, or place of origin, but rather by the specificity of each species.

The acute HC_5 value of imidacloprid for aquatic organisms in this study was 6.57 µg/L (95% CI: 1.18–76.49 µg/L), representing the concentration predicted to affect 5% of the species present in the aquatic community. That is, when this concentration is exceeded, adverse effects may occur in more than 5% of aquatic species. In Brazilian ecosystems, imidacloprid concentrations range from 0.01 to 3.65 µg/L (Bortoluzzi et al. 2006; Becker et al. 2009; Sequinatto et al. 2013; Sposito et al. 2018; Amaral et al. 2020; Gonçalves et al. 2020; Severo et al. 2020; Acayaba et al. 2021). Given these concentrations lower than the HC_5 value, in the central scenario, the values obtained were RQ < 1, indicating low acute community risk for most species – 3.65 µg/L does not reach the EC50 (acute). In the most sensitive scenario (lower 95% CI), the maximum RQ was (3.09), being greater than 1 (> 1), indicating potential ecological risk. In this scenario, the model indicates that more than 5% of the species may suffer adverse acute effects at the concentrations observed in the environment. And in the least sensitive scenario (upper 95% CI), the RQ values were lower than 1, indicating no significant ecological risk.

The results indicate that some aquatic organisms are exposed to an acute risk from imidacloprid, especially ostracod species. As the toxicity of imidacloprid varies strongly among different species, it is necessary to go beyond analyses based on *Daphnia* and to broaden the assessment of effects in order to better understand the ecological risk and the complex dynamics of communities affected by the presence of agrochemicals in the environment. In a previous ecological risk assessment (ERA) based on species sensitivity distributions (SSDs) for imidacloprid, Alexandre et al. (2025) estimated an HC_5 of 1.52 µg/L for tropical species and 0.44 µg/L for temperate species, demonstrating that the response to imidacloprid is strongly species-dependent. Within this assessment, the less sensitive tropical organisms were larger taxa such as anurans, fish, and rotifers, whereas the most sensitive were the insect *Chironomus sancticaroli* and the crustaceans *H. meinerti* and *S. rondoniensis*.

For temperate species included in the same SSD analysis, the highest sensitivity was observed in aquatic insects particularly *Epeorus longimanus*, *Chironomus tepperi*, and *C. dilutus* as well as in the cladoceran *Daphnia pulex*. In contrast, fish species such as *Lepomis macrochirus*, *Oncorhynchus mykiss*, and *Leuciscus idus* were among the least sensitive taxa. The risk analysis based on environmental concentrations of imidacloprid in Brazilian aquatic ecosystems indicated a high ecological impact on aquatic biota (Alexandre et al. 2025).

Feeding assay (ingestion rate) with *Ceriodaphnia* spp. and *Daphnia* spp.

The results showed different responses in the ingestion rates of the tested species during the period of exposure to imidacloprid. The insecticide did not significantly alter the ingestion rates of *D. similis*, *D. magna*, and *C. dubia*; however, for *C. silvestrii*, exposure to a concentration of 0.1 mg L^{-1} caused inhibition of ingestion rates. These results show that the feeding parameter can increase or decrease depending on the concentration, reflecting physiological responses, especially under chemical stress. In cladocerans, functions such as oxygen consumption, filtration, and feeding are directly linked to the movement of the thoracic appendages. The more intense these movements, the higher the filtration rates tend to be, as a response to physiological stress, acting as a detoxification mechanism (Araujo et al. 2019).

This feeding inhibition effect was observed in the mayfly *Epeorus longimanus* Eaton and in the oligochaete *Lumbriculus variegatus* when exposed to imidacloprid at concentrations higher than 0.5 but lower than 10 µg/L. In addition to the inhibition of feeding, imidacloprid reduced the survival and ingestion of the organisms. This inhibition of feeding and ingestion indicated physiological and behavioral responses of organisms exposed to this insecticide (Alexander et al. 2009). The reduction in feeding activity may result in a decrease in the energy that would be used and allocated to growth and reproduction, but this becomes compromised due to a lower retention of food particles during the filtration process of the individuals. This is in agreement with previous studies that observed that a 24-hour exposure to concentrations of 0.3 mg/L of fenvalerate (an insecticide) caused individuals of *D. magna* to filter and assimilate significantly less food (algae), resulting in smaller individuals (Reynaldi et al. 2006).

Moruzzi et al. (2025) compared the feeding responses of the cladocerans *C. silvestrii* and *C. dubia* exposed to agrochemicals at concentrations ranging from 0.4 to 2.0 µg/L for fipronil and from 40 mg/L to 80 mg/L for 2,4-D. The cladoceran *C. silvestrii* showed a response opposite to that observed in this study, that is, for both compounds there was an increase in the filtration and algal ingestion rates. It is more likely that inhibition of feeding rates occurs after exposure to a contaminant (Loureiro et al. 2010) than an increase in the capacity to ingest food; the latter may represent a survival attempt of the species in response to a contaminant (Araújo et al. 2019). In another study that evaluated the ecotoxicological effects of vinasse and the commercial agrochemicals DMA® 806 BR (herbicide) and Regent® 800 WG (insecticide), applied alone and in mixture, no defined pattern

in the feeding of *C. silvestrii* was observed among the treatments. In the case of the insecticide, it was observed that *C. silvestrii* doubled its filtration rates compared to control organisms, and in the herbicide treatments, when compared to the control, filtration rates were lower in one test but higher in another (Silva 2022).

Similarly, to the results of the present study, Gallo et al. (2023) did not observe significant changes in the ingestion rates of *D. similis* exposed to concentrations of 4, 8, and 16 µg a.i. L^{-1} of fipronil and 0.1, 0.5, and 1 mg a.i. L^{-1} of 2,4-D. This may indicate interspecific tolerance and a less impactful mode of action on the filtration process of this species. In contrast, in a feeding study with *D. magna*, algal feeding rates were inhibited after exposure to the fungicide tebuconazole. Ingestion rates were reduced at all concentrations of the fungicide, with the highest concentration used (1.14 mg/L) producing a reduction of 34% and 54% in filtration and ingestion rates, respectively (Sancho et al. 2009). Regarding the effects of pesticides on feeding rates in cladocerans and the responses observed in different studies, *D. magna* showed a decrease in filtration/ingestion rates when exposed to the insecticide cypermethrin and the fungicide azoxystrobin (Friberg-Jensen 2010), to the insecticide carbaryl (De Coninck et al. 2013), to procaine penicillin (an antibiotic) (Bownik et al. 2019), and to potassium dichromate ($K_2Cr_2O_7$) (McWilliam and Baird 2002). *D. similis*, in turn, often did not show alterations under the conditions tested with the insecticide fipronil and the herbicide 2,4-D (Gallo et al. 2023). *D. pulex*, although with few available records, showed a significant reduction in ingestion rates when exposed to the insecticide DDT and to glyphosate (herbicide) (Bengtsson et al. 2004). *C. silvestrii* also showed a negative response, but occasionally with no effect on filtration/ingestion rates when exposed to the insecticide fipronil and to the herbicide 2,4-D (Silva et al. 2020).

Chronic toxicity – Effects on reproduction

Exposure to imidacloprid reduced offspring production in *D. magna*, such that the number of neonates at all concentrations was significantly lower than in the control. However, the two highest concentrations (0.1 and 0.2 mg/L) showed numerically higher neonate production compared to the intermediate concentrations. Although these differences were not statistically significant among treatments, this pattern suggests a possible non-monotonic dose–response (NMDR), in which increases in dose do not necessarily correspond to proportional increases in biological effects. Similar responses have been reported for different compounds, particularly endocrine-disrupting chemicals, across several organisms (Hill et al. 2018).

The most frequent hypothesis proposed to explain NMDR profiles is the differential activation of multiple molecular targets (for example, hormonal receptors) that present distinct affinities for the same chemical substance. At low concentrations, the compound may act as a partial agonist, whereas at high concentrations it may exert an antagonistic effect (Lagarde et al. 2015). Another hypothesis proposed by some authors is the involvement of mechanisms mediated by G protein–coupled receptors (GPCRs) to explain this phenomenon. The decrease in GPCR sensitivity is a process in which receptors become less responsive to stimulation after prolonged or repeated exposure to a ligand, which could explain the reduction in system sensitivity with increasing concentration (Bossus et al. 2014; Guler and Ford 2010; Rivetti et al. 2016; Van der Most et al. 2024).

In the presence of stressors or low food availability, the female needs to trigger a change in reproductive strategy and redirect her energy either to produce more neonates that are smaller and more fragile, or fewer neonates that are larger and more robust (Gorbi et al. 2011). Therefore, growth and the duration of development may be related to energy demand. This is illustrated by the study of Cárdenas and Jerónimo (2012), who observed that as sublethal doses of hexavalent chromium increased in adults of *D. schodleri*, they induced a reallocation of energy to their offspring as a way to ensure neonate survival in a contaminated environment. Gottardi et al. (2017) observed that *D. magna* exposed to the fungicide epoxiconazole initially allocated its energy to growth and reproduction. Once survival is ensured, resources can be allocated to reproduction (Bradley et al. 1991). This is

consistent with the results of the present study when analyzing the effects on reproduction, in which the two highest concentrations showed numerically higher neonate production in *D. magna* compared to the intermediate concentrations, although no statistically significant differences were observed among treatments.

D. similis showed a significant reduction in neonate production after 15 days of exposure to imidacloprid at three concentrations (0.025, 0.1 and 0.2 mg/L) compared to the control. Based on these responses, effective concentrations were estimated, resulting in EC_{10} = 0.0001 ± 0.0003 mg/L, EC_{20} = 0.001 ± 0.003 mg/L and EC_{50} = 0.27 ± 0.20 mg/L. In the present study, the EC_{10}, EC_{20}, and EC_{50} estimated for *D. similis* exposed to imidacloprid were considerably lower than the NOEC (0.068 mg/L) and LOEC (0.136 mg/L) reported by (Tessaro 2023). Even though a reduction in reproduction was observed at the lowest concentration of 0.068 mg/L, and at concentrations ≥ 0.427 mg/L there were practically no offspring. Similar results were also found by Araújo et al. (2019), who compared the sensitivity of *D. similis* and *D. magna* exposed to lead (Pb) and mancozeb (an organic fungicide) over several generations, and found that *D. similis* was more sensitive to Pb than *D. magna* for several parameters. Regarding the fungicide, it caused negative effects in both species, including a decrease in reproduction, a reduction in population growth rate, a decrease in feeding assay, and an increase in AChE activity in both species. Oxygen consumption increased only in *D. magna*, whereas *D. similis* showed no effect under exposure to mancozeb. These differences in sensitivity observed between *D. similis* and *D. magna* to lead and to mancozeb demonstrate that species sensitivity, even among phylogenetically close species, is dependent on the parameter being evaluated.

Conclusions

The results of this study demonstrate that the insecticide imidacloprid (Imidagold 700 WG) presents differentiated acute and chronic toxicity among species, with interspecific variability in sensitivity. In the acute toxicity tests (48 h), the species *C. silvestrii* and *C. dubia* were more sensitive than *D. similis* and *D. magna*, especially *D. magna*, which showed a significantly higher EC_{50} value.

The acute species sensitivity distribution (SSD) curve (EC_{50}–48 h; 14 species) indicated an HC_5 of 6.57 µg/L. The ecological risk assessment based on these values revealed that, in the central scenario, the risk quotients (RQ) indicate insignificant to moderate risk for aquatic species. However, in the most sensitive scenario (lower 95% CI), the RQ values exceeded unity (RQ > 1), indicating a high potential ecological risk for aquatic organisms in relation to the maximum environmental concentrations of imidacloprid reported in Brazil.

In the feeding assays (24 h), *C. silvestrii* was the only species that showed a significant reduction in algae intake at a concentration of 0.1 mg/L of imidacloprid. These results characterize an acute sublethal response, showing that the effects of the insecticide are already detectable in short periods of exposure and that it is specific to each species.

In chronic tests with *D. similis* and *D. magna*, imidacloprid caused a significant reduction in reproduction in both species, especially in *D. magna* at the highest concentrations. For these species, reproduction proved to be a more sensitive parameter than feeding, showing that some effects may not be detected in short-term exposures, but only over longer periods.

In an integrated manner, the results demonstrate that sensitivity to imidacloprid varies among species and strongly depends on the ecotoxicological parameter evaluated. The inclusion of native species, such as *C. silvestrii*, as well as other groups such as Ostracoda and Cyclopoida, proved essential, since these organisms showed greater sensitivity to the insecticide when compared to the standard species *D. magna*. Thus, the selection of species or even a wide range of taxa in ecotoxicological assessments is crucial in evaluating ecological risk and defining water quality criteria.

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Declarations and Statements

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Competing Interests

The authors have no relevant financial or non-financial interests to declare.

Author Contributions

All authors contributed to the conception and planning of the study.

The experimental design and preparation of materials were carried out by Karen Pinheiro Lackman, Jeniffer Silveira Moraes, Raquel Aparecida Moreira, and Camila de Martinez Gaspar Martins. The methodology and laboratory analyses were performed by Lurian Aparecida Domingos da Cruz and Cassiana Carolina Montagner. Data analysis was performed by Karen Pinheiro Lackman. The first version of the manuscript was written by Karen Pinheiro Lackman, and all authors commented on previous versions. All authors read and approved the final version of the manuscript.

Supplementary Material

Capítulo 2

Species-specific sensitivity to imidacloprid: ecotoxicological effects on congeneric cladoceran and ecological risk assessment

Table S1. Names of the species that were used to construct the species sensitivity distribution (SSD) curve according to the acute toxicity values (EC50/LC50 (µg/L)) of the insecticide imidacloprid, the group to which they belong, and the references for each one.

IMIDACLOPRIDO			
Scientific name of species	**Group**	EC_{50}/LC_{50} (µg/L)	**Reference**
Cypridopsis vidua	Ostracoda	3.00	Bower e Tjeerdema (2019)
Cyprietta seuratti	Ostracoda	16.00	Bower e Tjeerdema (2019)
Tropocyclops sp.	Cyclopoida	15.50	Suzuki et al (2024)
Thermocyclops crassus	Cyclopoida	205.15	Suzuki et al (2024)
Thermocyclops taihokuensis	Cyclopoida	361.90	Suzuki et al (2024)
Mesocyclops sp.	Cyclopoida	500.00	Suzuki et al (2024)
Cyclops vicinus	Cyclopoida	554.05	Suzuki et al (2024)
Macrocyclops fuscus	Cyclopoida	830.02	Suzuki et al (2024)
Diaphanosoma cf. macrophthalm	Cladocera	123.82	Suzuki et al (2024)
a	Cladocera	405.32	Suzuki et al (2024)
Ceriodaphnia cf. lacustris			
Ceriodaphnia silvestrii	Cladocera	1500.00	This study
Ceriodaphnia dubia	Cladocera	16.40.00	This study
Daphnia similis	Cladocera	2350.00	This study
Daphnia magna	Cladocera	30850.00	This study

Table S2. Literature data on environmental concentrations of imidacloprid (IMI) recorded in surface waters from Brazil. MEC = measured environmental concentration.

Brazilian states	MEC minimum (µg/L)	MEC maximum (µg/L)	References
Rio Grande do Sul (microbacia de agudo)	0.38	2.18	Bortoluzzi et al. 2006
Rio Grande do Sul (Riacho Lino)	0.67	3.65	Becker et al. 2009
Rio Grande do Sul (bacia do rio Jacuí)	0.13	1.66	Sequinatto et al. 2013
Mato Grosso do Sul (bacia do Alto Paraná)	0.0239	0.0314	Sposito et al. 2018
Rio Grande do Sul (reservatório bacia do Alto Jacuí)	0.02	0.05	do Amaral et al. 2020
Rio Grande do Sul (Rio Uruguai)	0.01	0.07	Gonçalves et al. 2020
Rio Grande do Sul (Rio Vacacaí)	0.026	0.821	Severo et al. 2020
São Paulo (Região canavieira)	0.0067	2.579	Acayaba et al. 2021

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CONSIDERAÇÕES FINAIS E PERSPECTIVAS

Esta dissertação integrou o monitoramento ambiental de contaminantes na bacia hidrográfica da Lagoa Mirim com a avaliação ecotoxicológica do inseticida imidacloprido em organismos zooplanctônicos. Antes da realização deste estudo, o conhecimento disponível para a região estava concentrado principalmente em parâmetros físico-químicos, microbiológicos, metais e avaliação de agrotóxicos (somente 1 trabalho), havendo ainda poucas informações sobre contaminantes emergentes e/ou ambientais e seus possíveis efeitos biológicos. Assim, esta dissertação contribuiu ao combinar dados de ocorrência ambiental, revisão sistemática da literatura, ensaios laboratoriais e avaliação de risco ecológico.

No primeiro capítulo, a detecção de 22 dos 26 compostos analisados em águas superficiais da Lagoa Mirim demonstrou que esse sistema está exposto a uma mistura de substâncias associadas a diferentes fontes de contaminação, incluindo herbicidas, inseticidas, fungicidas, metabólitos de herbicidas, cafeína e antibiótico. A presença desses compostos em diferentes períodos do ciclo do arroz irrigado, inclusive na entressafra, indica que a entrada de contaminantes pode ocorrer de forma contínua ou resultar da persistência ambiental e de múltiplas fontes, como atividades agrícolas, ocupação humana e dinâmica hidrológica da bacia. A revisão sistemática também evidenciou a escassez de estudos sobre contaminantes emergentes na Lagoa Mirim, reforçando a importância de ampliar o monitoramento ambiental nesse sistema transfronteiriço.

No segundo capítulo, os ensaios com imidacloprido demonstraram efeitos letais e subletais em cladóceros, com diferenças interespecíficas de sensibilidade. A espécie nativa *Ceriodaphnia silvestrii* foi a mais sensível nos testes agudos e apresentou redução da taxa de ingestão, enquanto *Daphnia similis* e *Daphnia magna* tiveram redução na reprodução após exposição crônica. Esses resultados indicam que o imidacloprido pode afetar processos ecológicos essenciais do zooplâncton, como alimentação e reprodução, com possíveis consequências para a estrutura das comunidades aquáticas e para a transferência de energia nas cadeias tróficas.

De forma geral, os resultados reforçam que a avaliação da qualidade da água deve integrar a detecção química de contaminantes com estudos ecotoxicológicos, especialmente em bacias agrícolas e de importância ecológica e social. Como perspectivas, recomenda-se ampliar o monitoramento temporal e espacial da Lagoa Mirim, incluir organismos nas análises, avaliar misturas de contaminantes detectados no ambiente e incorporar espécies nativas de diferentes grupos taxonômicos em testes crônicos, subletais e multigeracionais. Essas abordagens poderão subsidiar programas de monitoramento contínuo, avaliações de risco e estratégias de gestão integrada dos recursos hídricos.