Comprehensive assessment of micropollutants in stormwater runoff from industrial and urban sites using suspect and non-target screening

Caractérisation globale des micro-polluants dans les eaux de ruissellement industrielles et urbaines au Luxembourg par analyse ciblée et non ciblée

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RÉSUMÉ

Les eaux de ruissellement transportent une grande variété de contaminants provenant de sources urbaines, industrielles et automobiles, mais nombre d'entre eux ne font l'objet d'aucune surveillance en raison de la difficulté de leur analyse. Dans cette étude, un profil complet de la pollution a été établi de deux filtres plantés (RSF) situés au Luxembourg. Les sites sélectionnés sont : (i) Raemerich, influencé par les activités industrielles et le trafic routier, et (ii) Grass Steinfort, représentatif des eaux de ruissellement issues des routes et des toitures. Les premières eaux de ruissellement collectées ont été analysées selon les paramètres classiques de qualité de l'eau, ainsi que par la détection de composés chimiques suspects et non ciblés. Les résultats préliminaires montrent que les eaux de ruissellement à Raemerich sont fortement polluées, avec des valeurs de DCO (0-175 mg/L) et de MES (2-1378 mg/L) nettement supérieures à celles de Steinfort. Les polluants inorganiques, en particulier Na^+, Cl^-, SO_4^{2-}, Br^- et Mg^{2+}, étaient systématiquement plus élevés, avec des pics lors des épisodes de lessivage induits par les précipitations. Les métaux préoccupants comprenaient notamment le Mo, le Ni et le V, atteignant respectivement 14, 16 et 6 mg/L. L'analyse suspecte a permis de détecter huit contaminants prioritaires à Raemerich, identifiés avec un niveau de confiance de 2a à 3a/3c, révélant la diversité des sources de pollution. Les marqueurs industriels 5-méthyl-1H-benzotriazole et tributylphosphate étaient particulièrement présents. Des produits pharmaceutiques tels que l'ibuprofène et la lidocaïne, ainsi que des pesticides comme le propiconazole et l'isoproturon, ont également été détectés. Des teneurs plus faibles mais récurrentes de DEET et de bisphénol A-d16 témoignent d'une contamination urbaine diffuse. Plusieurs contaminants clés persistaient au passage des filtres, montrant que les technologies de traitement actuelles sont insuffisantes et nécessitent des améliorations.

ABSTRACT

Stormwater runoff transports contaminants from urban infrastructure, automotive wear, industrial activities, and other sources into water bodies, while conventional monitoring focuses on known pollutants, leaving many emerging or unregulated compounds undetected. To obtain a comprehensive pollution profile, two retention-soil-filter (RSF) sites in Luxembourg were selected. (i) Raemerich, influenced by industrial and vehicular activities, and (ii) Grass Steinfort, representing road and rooftop runoff. First flushes were collected and analyzed for conventional water quality parameters, followed by combined suspect and non-target screening. Preliminary results show Raemerich runoff is heavily polluted, with COD (0-175 mg/L), and TSS (2-1378 mg/L) far exceeding levels at Steinfort. Inorganic pollutants including Na^+, Cl^- , SO_4^{2-} , Br^- , and Mg^{2+} were consistently higher than Steinfort, peaking during rainfall-driven wash-off. Metals of concern included Mo, Ni, and V, reaching 14, 16, and 6 mg/L, respectively. Suspect screening detected eight priority contaminants at Raemerich (2a-3a/3c confidence), highlighting diverse pollution sources. Industrial markers 5-methyl-1H-benzotriazole and tributyl phosphate were prominent in inlet and RSF effluent, while pharmaceuticals (ibuprofen, lidocaine) and pesticides (propiconazole, isoproturon) were also observed. Lower but recurrent levels of DEET and Bisphenol A-d16 reflected general urban contamination. RSF effluent showed reduced intensities, for ibuprofen, lidocaine, and isoproturon, suggesting partial attenuation. However, key contaminants persisted in RSF effluent, showing that RSF inadequately remove micropollutants and require optimization.

KEYWORDS

Emerging Micropollutants, First flush, Non-target screening , Stormwater runoff, Suspect Screening

1 INTRODUCTION

Stormwater runoff significantly impacts receiving water bodies, with its quality degraded by chemicals from pesticides, biocides, urban infrastructure, automotive wear, industrial discharges, and urban sources. Environmental monitoring focuses mainly on 'known' pollutants with available analytical standards, leaving many unregulated and undetected due to gaps in stormwater surveillance (Aurich et al. 2023). The European Union (EU) addressed these challenges by revising its priority substances list in 2022, adding 25 emerging contaminants including 6ppd-quinone (a tire wear derivative), while the 2023 Urban Wastewater Treatment Directive enforces the need for comprehensive monitoring and accountability of stormwater and combined sewer overflows, reflecting a shift towards integrated management of diffuse and wet-weather pollution (EU WWTD directive 2023, EU WWTD directive 2022). This issue is particularly critical in Luxembourg, with a high population density of ~260 inhabitants per km², where rapid urbanization, extensive impervious surface coverage, and industrial activities contribute to increased stormwater runoff volumes and pollutant loading (Douinot et al. 2022). To address these challenges, our project STORMland, funded by the Luxembourg National Research Fund (FNR), aims towards (i) developing a comprehensive stormwater monitoring approach of stormwater runoff, (ii) analyzing the distribution of stormwater contaminants in dissolved and particulate fractions across various particle sizes, and (iii) design a novel constructed stormwater wetland (CSW) with tailored substrates for targeted pollutant removal.

2 MATERIAL AND METHODS

Two monitoring sites have been selected for STORMland: (i) Raemerich (Fig. 1. (a)), located at the Luxembourg-France border, which exclusively collects stormwater runoff from a motorway managed by Administration des Ponts et Chaussées. This site has been designed with a retention soil filter especially for treating solids present in stormwater runoff. The Raemerich site has a total catchment area of 16.8 ha (168,000 m²) and is divided into three inlets: Inlet channel 1 (IC1) covers ~12% of the catchment (2.01 ha), Inlet channel (IC2) 2 ~55% (9.24 ha), and Inlet channel 3 (IC3) ~33% (5.54 ha). The total retention volume of the site is approximately 3,900 m³, with a total leakage/outflow of 28.5 L/s. (ii) Grass-Steinfort (Fig. 2. (b)), situated at the Luxembourg-Belgium border, which receives runoff from both urban roads and rooftops managed by Municipality of Steinfort. The Grass Steinfort site has a total catchment area of 17 ha, divided into three inlets: Inlet 1 covers 1 ha (10,000 m²), Inlet 2 covers 14 ha (140,000 m²), and Inlet 3 covers 2 ha (20,000 m²). The site includes two constructed wetland (area of 3,400 m²) and retention volume of 3,240 m³ with four outlets (CW1, CW2, CW3 and CW4), and a pond of 6,000 m² with a volume of 2,421 m³ and a depth of 1.5 m. Field campaigns were conducted in both winter and summer to collect first-flush stormwater runoff samples using autosamplers.

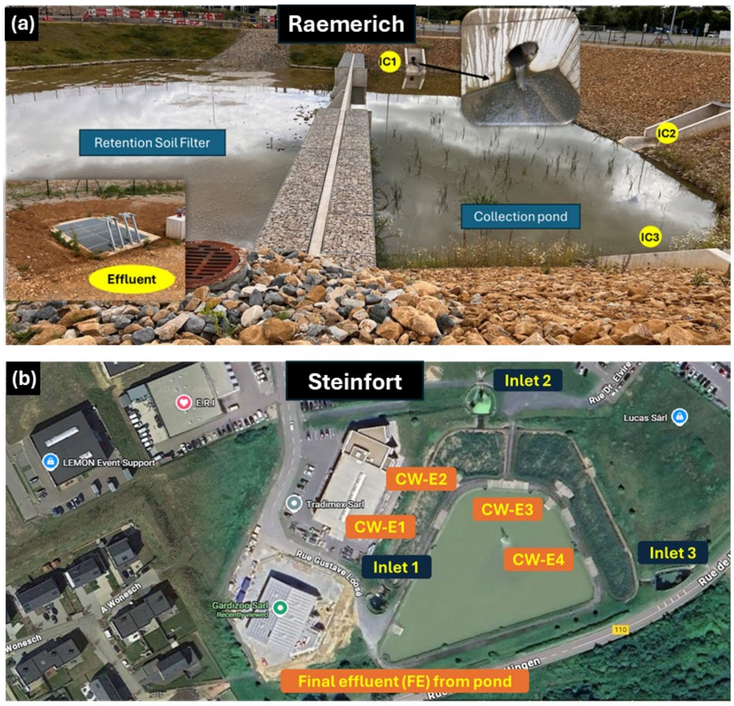

Fig. 1. Stormwater runoff sites (a) Raemerich (b) Steinfort

Initially, samples were analyzed for Physicochemical parameters (pH, conductivity, DO, redox & total suspended solids), Organic pollutants (COD_{total}, TOC, TC), Nutrients (NH_4^+, NO_3^-, NO_2^-, TN & PO_4^{3-}) , Inorganic pollutants (salts and ions mainly as Na^+, Cl^-, SO_4^{2-}, Ca^{+2} & Br^-) and microbiological analysis. Heavy metals were analyzed using ICP-OES. Then the collected samples were freezed at -20˚C and later processed for solid phase extraction. SPE samples were preserved with phosphoric acid, and spiked with internal standards such as Carbamaxepine-d10, Diclofenac-d4, Calrithromycin-d3, 1H benzotriazole (Sanbio, DE). The SPE cartridges were conditioned with 8 mL of methanol followed by 8 mL of Milli-Q water prior to sample loading. Subsequently, 250 mL of Raemerich samples and 500 mL of Steinfort samples were passed through the cartridges dropwise. After sample loading, the cartridges were dried under nitrogen and eluted with 8 mL of methanol. The methanol eluates were analyzed by LC-MS/MS for suspect screening, followed by full non-target screening. Suspect screening targeted a set of 194 preselected compounds aligned with national protocols of the water administration.

Data processing and evaluation were performed using the R statistical environment, where peak intensities from the suspect-screening workflow were compiled, cleaned, and normalized against corresponding blank samples across all grab and autosampler samples. Suspect annotations were first generated using MoNA (MassBank of North America) spectral match scores and corresponding confidence intervals, which served as the initial criteria for ranking and filtering potential compounds. All preliminary annotations were subsequently verified manually in Xcalibur by inspecting extracted ion chromatograms (EICs), retention times, isotopic patterns, and MS/MS fragmentation quality. For further structural confirmation, each candidate compound was re-evaluated using MetFrag Web, employing in silico fragmentation matching against relevant databases to strengthen the level of confidence according to established identification frameworks (e.g., Schymanski levels). Only compounds that fulfilled all spectral, chromatographic, and fragmentation criteria across these steps were retained as confirmed suspects for interpretation. This combined computational and manual validation approach ensured robust, high-quality chemical identification across complex stormwater matrices (Aurich et al. 2023).

3 RESULTS AND CONCLUSIONS

During the winter sampling campaign, a total of 32 grab samples and 25 autosampler samples were collected from the three inlet channels and the retention-soil-filter effluent at Raemerich. At Steinfort, 44 grab samples and 29 autosampler samples were collected from the three inlet channels, four constructed wetland effluent channels, and the final pond outflow. During the summer campaign, the combined number of grab and first-flush samples totaled 36 samples for Raemerich and 52 samples for Steinfort.

Preliminary findings from Raemerich indicate that first-flush stormwater runoff is highly contaminated as seen in Fig. 1. (a) (Maniquiz-Redillas et al. 2022). Conductivity ranged from 641-3870 µS/cm, chemical oxygen demand (COD) from 0-175 mg/L, total suspended solids (TSS) from 2-1378 mg/L, and volatile suspended solids (VSS) from 5.2-154.56 mg/L (Göbel et al., 2007). Minimum values were consistently observed during dry periods, whereas peak concentrations occurred during runoff events. As seen in Fig. 2. (b), inorganic pollutant levels were also significant, with elevated concentrations of Na^+ (24.8-689.3 mg/L), Cl^- (28.8-1271 mg/L), SO_4^{2-} (38.44-4444.3 mg/L), Ca^{2+} (18.51-604.2 mg/L), Br^- (0.263-3.99 mg/L), and Mg^{2+} (0.1642-44.81 mg/L). High Na^+, Cl^-, and Ca^{2+} concentrations are likely influenced by de-icing salt applications, elevated SO_4^{2-} by mining activities in the south of Luxembourg, and Br^- potentially by dibromoethane fuel additives (Makepeace et al. 1995; Sollars et al. 1982). In contrast, Steinfort exhibited much lower pollutant loads. Conductivity ranged from 228-833 µS/cm, COD from 0-22 mg/L, and TSS from 0-190 mg/L. Inorganic ion concentrations remained comparatively low: Na^+ (15.5-38.2 mg/L), Cl^- (36.5-115.3 mg/L), SO_4^{2-} (57.2-115.77 mg/L), Ca^{2+} (31.5-57.6 mg/L), Br^- (0-0.86 mg/L), and Mg^{2+} (0.86-6.45 mg/L).

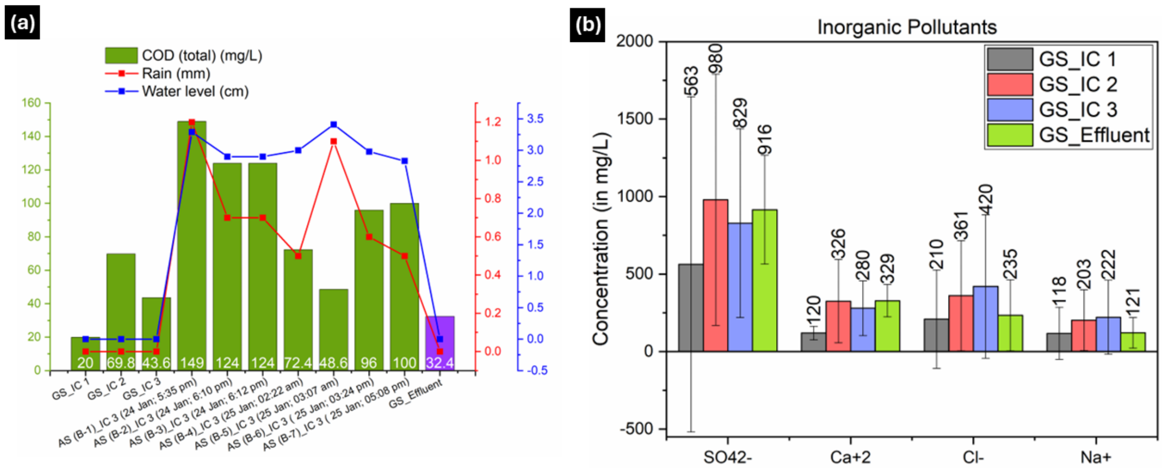

Fig. 2. (a) Corellation of COD, water level and rain in Raemerich inlet channel 3 (IC3) (b) Concentration of inorganic pollutants in inlets and effluent channels in Raemerich. Where, AS: autosampler; GS: grab sample; B: bottle of autosampler.

Metal analysis identified molybdenum (Mo), nickel (Ni), and vanadium (V) as contaminants of highest concern. Across the three inlet channels in Raemerich, mean concentrations ranged from 9.41 ± 2.57 to 13.99 ± 0.37 µg/L for Mo, 5.71 ± 0.83 to 15.98 ± 3.82 µg/L for Ni, and 4.90 ± 0.60 to 5.59 ± 0.27 µg/L for V. The retention soil filter effluent showed higher variability, with average concentrations of 16.47 ± 1.94 µg/L (Mo), 12.52 ± 6.04 µg/L (Ni), and 1.86 ± 0.50 µg/L (V). Overall, the effluent displayed greater fluctuations and distinct metal signatures compared to I1, I2, and I3 (Göbel et al. 2007). Additionally, microbial analysis revealed high contamination levels of total coliforms and *E. coli* (Shubo et al. 2022). The observed pollutants/contamination levels in this Raemerich surpass previously reported stormwater runoff data from high-traffic areas, highlighting the significant pollution load associated with these urban runoff sources (Göbel et al. 2007).

The suspect-screening analysis of grab and autosampler stormwater samples from the Raemerich winter campaign revealed distinct occurrence patterns and source signatures across compounds, influenced by measured water levels (2.8-6.3 mm). The industrial corrosion inhibitor 5-methyl-1H-benzotriazole was consistently detected at high intensities (3×10^7-6×10^7) across nearly all inlet channels and effluent, with particularly strong signals at the highest water levels (≥6 mm), corresponding to intense first-flush conditions, confirming persistent inputs likely linked to vehicular and industrial activities (Aurich et al. 2023). Tributyl phosphate, a solvent and plasticizer, showed widespread, elevated signals at medium water levels (~3-4 mm), indicating continuous industrial or material-related loading independent of flow stage. Pharmaceuticals exhibited sporadic occurrences: ibuprofen was mainly detected in the IC3 inlet, with strongest signals at lower water levels (~2.9 mm), suggesting episodic or delayed arrival during later runoff stages. Lidocaine appeared in single grab samples at similar low water levels, reflecting irregular, one-time inputs rather than continuous release (EU UWTTD 2033). Herbicides showed varied patterns: isoproturon occurred in IC1 and composite samples, with reduced effluent intensities under low-to-mid water levels, indicating diffuse catchment entry with partial RSF attenuation. Propiconazole displayed variable intensities, including occasional high peaks at mid-range water levels, consistent with intermittent agricultural or biocidal mobilization. DEET (N,N-diethyl-m-toluamide) varied moderately and was more prominent at lower water levels, reflecting delayed human-linked mobilization. Bisphenol A-d16, used as an internal standard, appeared only in IC1 and IC3, highlighting flow- and matrix-dependent recovery differences aligned with water-level stages (Aurich et al. 2023). Effluent samples generally exhibited reduced pharmaceutical and herbicide intensities, particularly ibuprofen, lidocaine, and isoproturon, confirming partial attenuation within the RSF at later runoff stages. Overall, industrial chemicals dominate the pollutant profile with continuous inputs regardless of flow intensity; pharmaceuticals are episodic and associated with low-water runoff; and herbicides/biocides reflect diffuse or seasonal mobilization. Integrating water-level dynamics with grab and autosampler data provides a detailed understanding of stormwater contamination. Full non-target screening, currently underway, will offer an even more comprehensive assessment of pollutants.

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