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Raising awareness on algal toxins—a discussion on potential pathways of microcystins to urban groundwater systems

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Abstract

Accelerated by urbanization, as well as by agricultural intensification and climate change, increasing nutrient fluxes towards surface waters and increasing water temperatures are increasing the probability for cyanobacterial harmful algal blooms. Significant deterioration of water quality occurs with such events when microcystins (MCs) are released as the most prominent algal toxins. Despite the typical assumption that MCs are removed during percolation, studies have found significant concentrations in groundwater bodies. In this article, advances and challenges associated with monitoring and modeling techniques for characterizing the fate of MCs are discussed. Missing insights in the mechanisms leading to elevated MC concentrations in the subsurface—ultimately limiting the reliability of risk assessments—are identified. An important aspect is the a priori identification of environmental conditions and corresponding events that support bloom formation in surface waters and subsequent transport into groundwater. Challenges associated with required improved monitoring and simulation techniques are formulated. In particular, the role of environmental conditions in urban regions as major drivers for heat and nutrient emissions controlling bloom formation, potentially limiting MC retardation, needs to be further investigated. Based on existing experimental studies on MC reactive transport in porous media, existing monitoring methods need to be refined and combined with suitable modeling approaches. A thorough data analysis can then support efforts for sustainable water management of urban regions under threat by algal toxins.

Keywords Microcystins · Urban groundwater · Harmful algal blooms · Cyanobacteria

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Sensibilisierung für Algentoxine – Eine Diskussion über mögliche Wege von Mikrocystinen in städtische Grundwassersysteme

Zusammenfassung

Beschleunigt durch Urbanisierung, landwirtschaftliche Intensivierung und den Klimawandel führen zunehmende Nährstoffeinträge und steigende Temperaturen in Oberflächengewässern zu einer erhöhten Wahrscheinlichkeit für schädliche Blaualgenblüten. Solche Ereignisse gehen mit erheblichen Verschlechterungen der Wasserqualität einher, insbesondere wenn Mikrocystine (MCs) – als die bekanntesten Algentoxine – freigesetzt werden. Trotz der gängigen Annahme, dass MCs während der Versickerung entfernt werden, wurden in Studien signifikante Konzentrationen in Grundwasserkörpern nachgewiesen. In diesem Artikel werden Fortschritte und Herausforderungen im Zusammenhang mit Monitoring- und Modelliertechniken zur Charakterisierung des Verbleibs von MCs diskutiert. Fehlende Erkenntnisse über die Mechanismen, die zu erhöhten MC-Konzentrationen im Untergrund führen – und somit bislang eine unzureichende Risikobewertung verursachen – werden identifiziert. Ein wichtiger Aspekt ist die frühzeitige Identifizierung von Umweltbedingungen und entsprechenden Ereignissen, die die Algenblütenbildung in Oberflächengewässern sowie den anschließenden Transport ins Grundwasser begünstigen. Die damit verbundenen Herausforderungen hinsichtlich verbesserter Monitoring- und Modelliertechniken werden herausgearbeitet. Insbesondere die Rolle der Umweltbedingungen in städtischen Regionen – als wesentliche Verursacher für Wärme- und Nährstoffemissionen, die die Algenblütenbildung fördern und potenziell die Rückhaltung von MCs erschweren – muss weiter untersucht werden. Basierend auf bestehenden experimentellen Studien zum reaktiven Transport von MCs in porösen Medien ist es erforderlich, bestehende Monitoringmethoden zu verbessern und mit geeigneten Simulationsansätzen zu kombinieren. Eine gründliche Datenanalyse kann dann die Bemühungen um ein nachhaltiges Wassermanagement in von Algentoxinen bedrohten urbanen Regionen unterstützen.

Schlüsselwörter Mikrocystine · Städtisches Grundwasser · Schädliche Algenblüten · Cyanobakterien

Introduction

A major threat for aquatic systems is given by increasingly occurring cyanobacterial harmful algal blooms (cHABs; Diez-Quijada et al. 2019; Vieira et al. 2024). Such events pose risks for ecosystems due to their potential to produce algal toxins of various types (Meriluoto et al. 2017). In particular, the group of microcystins (MC) can cause severe detrimental effects for livestock and humans (IARC 2010; Christen et al. 2013; Testai et al. 2016). In line with cHABs, the occurrence of MCs in water bodies has reached a global scale, ranging from cold (Paldaviciene et al. 2015; Namsaraev et al. 2020) to temperate (Harke et al. 2016; Xiang et al. 2019) to warm climates (Preece et al. 2017; Onyango et al. 2020).

Cities and urban regions in general have been historically located in close vicinity to surface water bodies (seas, lakes, streams) in direct exchange with subsurface fresh water systems (Fig. 1). A set of treatment steps in waterworks is common when withdrawing raw water. However, MC mitigation in water treatment plants is challenging and species-dependent (Crettaz-Minaglia et al. 2015). Conventional treatment procedures (e.g., filtration, chlorination, ozonation) can remove both cyanobacterial cells and cell-bound MCs but are limited to cases with organic loads during bloom season (Hitzfeld et al. 2000; Merel et al. 2013). More sophisticated methods are necessary for the removal of extracellular, water-dissolved MCs. Here, good removal efficiencies for selected MC species were achieved by, e.g., membrane filtration (Gijsbertsen-Abrahamse et al. 2006), activated carbon (Cook and Newcombe 2002), or biological filtration (Bourne et al. 2006; Ho et al. 2007).

MC sources and above-surface transportation vectors are partially evident already (Fig. 1). Untreated or poorly treated surface water or groundwater represents a source for drinking water (Tian et al. 2013) and for irrigating farmland (Jia et al. 2018; Xiang et al. 2019). Algal sludge and surface water sediments are used seasonally for the fertilization of crops or are intentionally disposed of (Chen et al. 2012; Yang et al. 2016). In consequence, MCs can be directly ingested by plants and crops (Jia et al. 2018), or they can temporally accumulate in soils and sediments (Lemes and Yunes 2017; Pham and Utsumi 2018). Despite natural MC biodegradation in surface water bodies, soils and sediments (Song et al. 2014), MC concentrations have recently been detected in urban parks (Vieira et al. 2024), groundwater samples (Chatziefthimiou et al. 2016; Yang et al. 2016; Abesh et al. 2022), and waterworks (Lahti et al. 2001; Pantelić et al. 2013). Given the complexity of cHAB and MC interaction, transition vectors and the spatiotemporal offset between MC sources and groundwater bodies are still insufficiently understood (Mutoti et al. 2023; Ahmad et al. 2025). This poses a potential threat to this essential water resource, including in urban regions largely depending on surface water (via bank filtration) and direct groundwater supply.

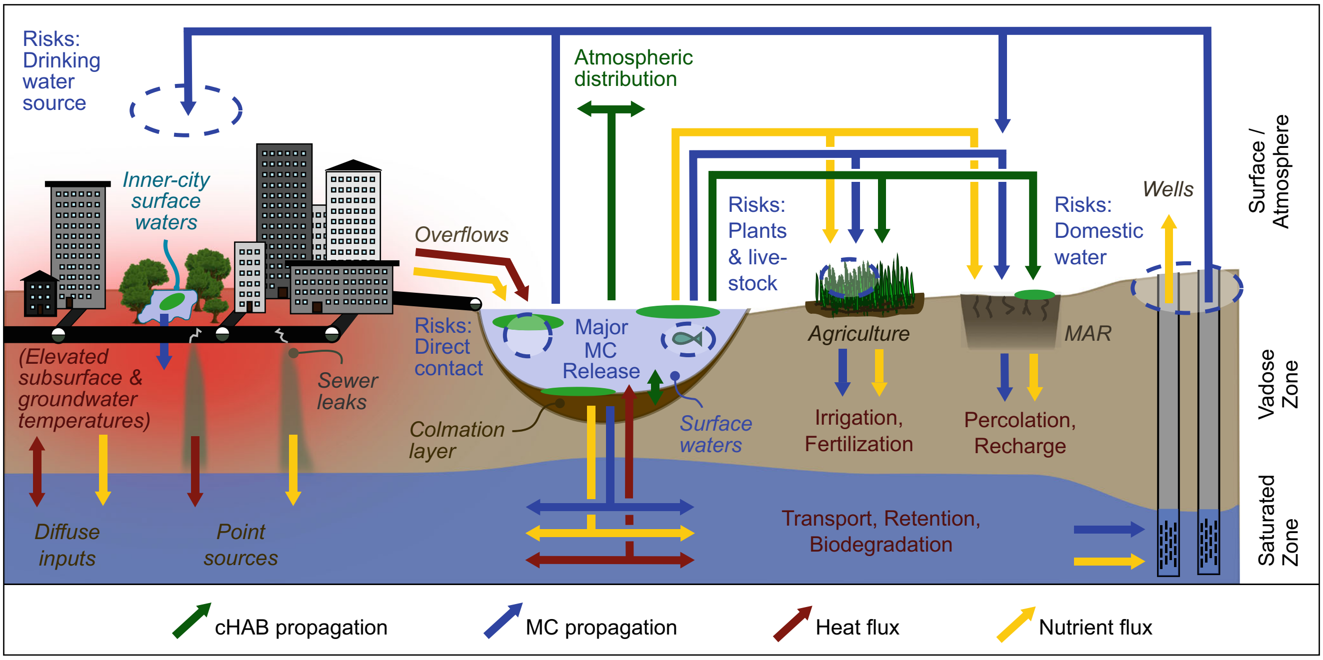

Fig. 1 Schematic concept of cyanobacteria distribution and MC contamination

Abb. 1 Schematisches Konzept für die Verteilung von Cyanobakterien und MC-Kontamination

In this study, MC pathways from sources to receiving water bodies are discussed. Furthermore, existing characterization methodologies covering monitoring-, experimental- and model-based approaches are presented. The study identifies key scientific questions and challenges for water management in urban regions, and suggests research demands that may lead to an improved understanding and prevention of MC contamination in groundwater.

Plausible MC transportation pathways

Background of MC occurrence

Eutrophication as a main driver for cHAB occurrence has significantly harmed the ecological conditions of many water bodies (Visser et al. 2016; Woolway et al. 2021). The primary causes are nutrient fluxes emerging from anthropogenic sources (e.g., agriculture, sewer networks, municipal wastewater outlets, and industries) as well as extreme weather events (Paerl and Paul 2012). This is further impacted by the ongoing climate crisis (IPCC 2023) involving temperature increases above and beneath land surfaces (Epting and Huggenberger 2013; Binder et al. 2025). Consequently, cHABs have been observed with increasing frequency and intensity (Nyachiro et al. 2016; Gorham et al. 2017). Following Wells et al. (2015), a shift of the potential for cHAB occurrence toward higher latitudes including mid-Europe is expected. MCs are commonly found in up to 75% of cHABs (Ettoumi et al. 2011) either cell-bound or in the free water column, and are caused by MC synthesis and release (e.g., Bortoli et al. 2014; Wang et al. 2018). Rural areas therefore typically act as MC source regions, while urban areas are MC-receiving entities (Fig. 1).

Factors influencing MC occurrence

Drivers that control cyanobacterial growth and cHAB formation under past and present environmental conditions are rather well known (O'Neil et al. 2012). On the other hand, the systematic or spontaneous release of cellular MCs into the surrounding water is insufficiently understood, especially for systems under the influence of complex environmental factors and interplays (Liu et al. 2012; Merel et al. 2013). Furthermore, exposure scenarios under changing conditions (urbanization, climate crisis) are currently unclear (Ahmad et al. 2025). Recent studies could identify individual factors influencing MC presence for selected MC species (Table 1); some of these factors such as presence of antibiotics, heavy metals and other contaminants are quite often associated with urban and industrial regions. Unfortunately, data about MC transport dynamics in the subsurface is limited to a few regions and to laboratory-scale investigations to date (Pham and Utsumi 2018). In the light of the subsurface urban heat island effect (Binder et al. 2025) that can significantly increase groundwater temperatures, a thorough understanding of temperature-dependent trans-

Table 1 Selected studies which identified drivers promoting cHAB formation as well as MC synthesis, release, and mobility under changing conditions caused by urbanization and climate change.
Tab. 1 Ausgewählte Studien, welche Verursacher für die Bildung von Blaualgenblüten sowie die Synthese, Freisetzung und Mobilität von MCs unter veränderlichen Bedingungen aufgrund von Urbanisierung und Klimawandel identifizierten.

Drivers		Correlation with	
Parameter	Expected future behavior	cHABs	MCs
Water temperature	Increase	Jiang et al. (2008), Kosten et al. (2012), Wagner et al. (2012), Jäschke et al. (2013), Visser et al. (2016)	None
Intensity of precipitation events	Increase	Reichwaldt and Ghadouani (2012)	None
Nutrient concentrations	Increase	Graham et al. (2004) Jiang et al. (2008) Gobler et al. (2016) Paerl et al. (2016)	Kotak et al. (1995), Rapala et al. (1997), Sivonen and Jones (1999), Oh et al. (2000) Downing et al. (2005), Kuniyoshi et al. (2013)
Atmospheric CO_2 concentrations	Increase	Qiu and Gao (2002), Visser et al. (2016)	None
Water pH values	Decrease	Qiu and Gao (2002), Visser et al. (2016)	None
Water body stratification periods	Increase	Walsby et al. (1997), Elliot (2010), Paerl and Paul (2012)	None
Salinity	Increase	Walsby et al. (2006), Paerl and Paul (2012)	None
Changed wind patterns	–	Wu et al. (2015)	None
Light intensity	Increase	Jiang et al. (2008)	None
Concentrations of heavy metals	Increase	Jiang et al. (2008)	Tao et al. (2015), Martínez-Ruiz and Martínez-Jerónimo (2016)
Low organic matter content of sediments	–	None	Tian et al. (2013), Yang et al. (2016)
Nonylphenol groups	Increase	Wang et al. (2007)	Wang et al. (2007)
Antibiotics	Increase	None	Liu et al. (2012)

port processes (Binder et al. 2021)—which might also affect MC mitigation—is essential.

Environmental monitoring

CHAB monitoring can be carried out through in-situ sampling, ex-situ laboratory analysis, and remote sensing (Erickson et al. 2011). While conventional, microscopic examinations are unable to detect short-term changes (Zamyadi et al. 2012), more recent technologies such as in-vivo fluoroscopy (Zamyadi et al. 2016) allow for in-situ, quasi-continuous cHAB monitoring (Catherine et al. 2013). Recent trends towards aerial-based sensors offer even more efficient monitoring possibilities (Stumpf et al. 2016; Clark et al. 2017), but are not capable of monitoring benthic cyanobacteria (Catherine et al. 2013).

MC detection techniques include biochemical methods coupled to spectral analysis (e.g., ELISA, HPLC, LC/MS, UPLC/MS, PPI; Gupta et al. 2024) with detection limits down to 0.1 µg l^{-1} (Shan et al. 2011; Merel et al. 2013; Schmidt et al. 2014). Recently developed techniques such as the real-time PCR test are capable of detecting the amount of MC genes to quantify the toxicity potential of a given cyanobacteria (Neilan et al. 2013). The automation of such techniques is a breakthrough for quasi-continuous monitoring (Merel et al. 2013). Initial semi-quantitative tests such as strip tests can further mitigate monitoring costs, but are limited to qualitative results on MC presence above typical guideline values (Humpage et al. 2012).

MC transport characteristics in the subsurface—the current knowledge

Field observations in transition zones and groundwater

Clogging layers, sediments and the vadose zone (Fig. 1) are important transition zones providing potential for increased retention times and chemical reactions (Massmann et al. 2004), thus potentially mitigating MC transport toward groundwater bodies. Studies have shown that maximum MC elimination occurs during the first few meters of subsurface migration (Dillon et al. 2002; Song et al. 2014), i.e., where availability of suitable electron acceptors (esp. oxygen and nutrients), organic sediment content, and usually higher silt/clay content (due to surface erosion processes) are beneficial conditions for MC mitigation from infiltrating water.

Under oxidizing conditions and with peak MC concentrations, removal efficiencies between 80 and 100% have been observed (Grützmacher et al. 2010), with MC usually being degraded within a few days (Jones et al. 1994; Bourne et al. 1996). Conversely, Chen et al. (2010) identified anoxic biodegradation as an effective removal pathway of MCs in lake sediments.

In some cases, there is evidence that transition zones such as colmation layers cannot efficiently protect groundwater against MC infiltration (Yang et al. 2006; Corbel et al. 2014). Once in groundwater, i.e., under fully water-saturated conditions, MC persistence in porous media then tends to be high with potential for significant spreading. For example, in raw water samples of Finnish bank-filtration sites, MC-LR concentrations up to 10 µg l^{-1} were measured (Lahti et al. 2001). In a study situated in northern China, concentrations up to approx. 0.4 µg l^{-1} were detected even in wells with depths of up to 400 m (Tian et al. 2013). For anoxic, denitrifying conditions present in water-saturated aquifers, dissimilative nitrate reduction can provide significant biodegradation rates (Holst et al. 2003; Stuart and Lapworth 2014). Some field studies observed that after 0.5 to 1 month of subsurface migration, MC concentrations usually fall below the World Health Organization advisory level of 1 µg l^{-1} MC-LR (WHO 1998; Chorus et al. 2006).

Characterization of MC mitigation processes

While MC concentrations in surface waters can be reduced through photodegradation, especially under the presence of humic substances (Van Apeldoorn et al. 2007), MC mitigation in the subsurface is mostly controlled by sorption and degradation (Chen et al. 2008; Maghsoudi et al. 2015). Sorption isotherms were experimentally determined for variable sediment types and MC species (Maghsoudi et al. 2015) whereby sorption behavior depended strongly on MC structure and pH value (Miller et al. 2005; Chen et al. 2006; Wu et al. 2011; Merel et al. 2013). A higher clay content is associated with stronger adsorption due to the larger surface area available for binding MC in comparison to more coarse fractions (Maghsoudi et al. 2015). While some studies raised doubts about the importance of organic matter for sorption (Dillon et al. 2002; Chen et al. 2006), Wu et al. (2011) state a non-linear relationship, where MC adsorption is increased at higher organic matter content. Depending on organic matter content, MC desorption as a toxin re-release effect may occur for such substrates (Miller et al. 2005). However, relatively low desorption rates have been observed (Maghsoudi et al. 2015). In general, however, sorption cannot be seen as a major MC elimination process in aquifers or sediments with low silt or clay content (Grützmacher et al. 2010).

Biodegradation of MC has been identified as a more relevant process over time (Holst et al. 2003; Gupta and Gajbhiye 2004). Like many other organic pollutants, a lag phase of several days can occur between the first MC input and the start of biodegradation (Jones et al. 1994; Edwards et al. 2008). The density of MC-degrading microorganisms is an important factor as well (Dillon et al. 2002). Several of these bacteria prefer neutral pH values but are also tolerant to higher values (Li et al. 2017). Nutrients can increase growth and activity of MC-degrading microorganisms, yet may become the preferable substrate thus inhibiting degradation (Li et al. 2017). Experimental studies found that MC biodegradation depends on temperature, with higher values between 25 and 30 °C being beneficial, and lower values often causing a slow-down or inhibition (Ho et al. 2007; Chen et al. 2010). This may indicate a higher likelihood for MC mitigation in subsurface porous media affected by the subsurface urban heat island effect (Fig. 1).

Laboratory results versus real-world assessments

High system complexities are given by multiple MC sources (Fig. 1), a range of MC variants that may show different transport behavior, and a large variety of environmental factors controlling relevant MC transport processes including infiltration, transport, sorption and degradation. The primary goal of recent experimental studies was to evaluate the sufficiency of typical raw water treatment technologies for MC mitigation from surface water under well-defined laboratory conditions. However, with evidence of MC occurrence in transition zones and groundwater at hand, MC behavior in real-world porous media must be evaluated as well. Experimental studies can aid in determining transport parameters, yet real-world data acquisition (MC monitoring) combined with site-scale reactive transport simulations is crucial. With MCs being water-dissolved organic chemicals, we hypothesize that an adoption of standard numerical reactive transport modelling systems is suitable and an implementation of modelling approaches analogous to the simulation of other non-conservative, water-soluble organic compounds is suitable.

Real MC transport simulations on regional scales barely exist to date. A conceptual workflow was presented by the NASRI project related to a study site near Berlin, Germany (Grützmacher et al. 2006). Here, MC degradation processes during bank filtration were investigated by a combination of hydrochemical monitoring, laboratory-scale experiments, and numerical modelling. Their geochemical field data showed MC concentrations below the detection limit, so that no field degradation rates could be estimated. Although a transient flow and multi-component, reactive transport model has been set up to simulate ammonium dynamics

(Nützmann et al. 2011), MC transport in groundwater was not simulated.

In general, the location of MC source terms, i.e., the cHABs and their fate, is a mandatory input dataset for correctly simulating MC transport behavior. A variety of models for population dynamics of cyanobacteria and bloom prediction, capable of simulating cHAB dynamics under given atmospheric boundary conditions and GIS data, exist to date (Serrano et al. 2015; Medrano et al. 2016; Rowe et al. 2016). However, these models do not describe MC synthesis and release into the surface water. Correlations between bacterial growth and MC synthesis/release were obtained for small-scale experimental results and need to be transferred to regional scales (Oh et al. 2000; Long et al. 2001). Existing sediment release models (Hu et al. 2011) may be adoptable for MC dynamics. For this, it is necessary to decrease the technical effort required for MC monitoring in transition zones and groundwater, to create a sound base for model calibration.

Challenges for improved water management

Some studies suggest implementing cHAB and MC monitoring in management guidelines officially prescribed by water authorities (Wood et al. 2009; Newcombe et al. 2010; Zamyadi et al. 2016; Ahmad et al. 2025). Consequently, pre-bloom information of monitoring programs may be used as an early warning system for MC exposure (Chang et al. 2012). One key challenge here is the current lack of a unique definition for a tolerable MC concentration. The World Health Organization has defined a provisional guideline value for acute toxicity based on an estimated tolerable daily consumption rate of 0.04 µg kg^{-1} (assumptions: security factor of 1000; 60 kg body weight; daily water consumption of 2 L; MC consumption ratio: 20% via food and 80% via drinking water; Fawell et al. 1994; WHO 1998). However, Dietrich and Hoeger (2005) argue that those values are inadequate for infants and children, and also issued the need for an additional uncertainty factor that considers MC's tumor-promoting capacity. The toxicological relevance is difficult to judge because the guideline value is not defined for individual MC variants (Chorus 2012). Schmidt et al. (2002) and Hoeger et al. (2005) point towards an alternative, provisional threshold value of 0.1 µg l^{-1} for toxic substances with unknown character that has been derived from the European Union's guideline value for pesticides. A threshold for chronic exposure has not been determined to date, yet intoxication hazard is not only given by direct water consumption, as MCs can accumulate in plants and livestock (Jia et al. 2018; Pham and Utsumi 2018).

Being a standard technique in water resource utilization, bank filtration is believed to safeguard the mitigation of hazardous organic compounds to tolerable concentrations in raw waters. Studies showed, however, that MC mitigation during subsurface pathways may be limited or unsuccessful depending on porous media and environmental conditions. Given contradictory and uncertain data on MC reactive transport behavior in porous media, this approach may not be a sufficient solution by default to lower MC concentrations to an acceptable level. In this context, also the existing definition of 50-day isochrones for delineating sufficiently large water protection zones appears questionable to date. As urban regions largely depend on a secure groundwater supply, the impacts of densely populated areas, which specifically promote cHAB formation through heat and nutrient fluxes on groundwater quality, need to be evaluated.

Conclusions

The threat of algal toxins in aquatic environments is a pressing issue in water management. The interplay of climate change and urbanization causes an increase of temperature and nutrients as primary drivers for algal blooms, including rising (sub)surface temperatures, season shifts, mobilization and abundance of nutrients, and extreme weather events. These external stressors lead to joint impacts promoting the likelihood, intensity and frequency of cHABs, and a shift of cHAB- and, hence, MC-affected regions towards moderate climates. With evidence for MC occurrence in groundwater bodies at hand, transition zones (e.g., lake sediments, vadose zones at managed aquifer recharge sites, bank filtration sites) may not prevent MC contamination of groundwater reservoirs that are exploited with increasing intensity as long-term sources of potable water.

Following this motivation, we draw these main conclusions:

1. A sound data basis identifying environmental conditions and corresponding events that support bloom formation in surface waters and subsequent MC transport into groundwater is key for identifying the current and future status of MC contamination. These data aid to improve the understanding of MC sources and transition vectors toward MC uptake regions. Existing monitoring networks and strategies are to be complemented by MC concentration detection, and analytical methods for MC concentration measurement are to be further simplified to enable widespread MC monitoring at reasonable economic expenses.
2. Past studies have implemented small-scale column and batch experiments to determine MC behavior in porous media. Given a wide range of open research questions on MC transport dynamics in the subsurface, standards for

laboratory experiments with controlled conditions (e.g., hydrochemical properties of porous media, MC species, physicochemical parameters such as temperature and pH) are needed.
3. Well-calibrated reactive transport models are prerequisites for predicting MC distributions and dynamics in transition zones and groundwater, and to support contamination risk prevention strategies for water management authorities. Supported by quasi-continuous field monitoring and laboratory-aided parameter quantification, transport models should be set up, calibrated, and verified. In parallel to standard numerical model systems, alternative methods (e.g., deep learning) may be considered to link the MC occurrence to environmental variables, as these can further simplify simulation efforts for regional scales.

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