

Water Resources Research

COMMENTARY

10.1029/2021WR029890

Andrea L. Popp, Cara C. M. Manning, and Julia L. A. Knapp contributed equally to this work.

Key Points:

- New mobile mass spectrometry (MS) systems enable low-cost, high-resolution dissolved gas measurements
- High-resolution sampling of dissolved gas tracers can provide new insights into hydrologic processes and systems
- Combining dissolved gas measurements with other experimental and numerical methods has the potential to further hydrological research

Correspondence to:

A. L. Popp, C. C. M. Manning, and J. L. A. Knapp,
andrea.popp@geo.uio.no;
cmanning@alum.mit.edu;
julia.l.knapp@durham.ac.uk

Citation:

Popp, A. L., Manning, C. C. M., & Knapp, J. L. A. (2021). Rapid advances in mobile mass spectrometry enhance tracer hydrology and water management. *Water Resources Research*, 57, e2021WR029890. <https://doi.org/10.1029/2021WR029890>

Received 26 FEB 2021

Accepted 20 MAY 2021

© 2021. The Authors.

This is an open access article under the terms of the [Creative Commons Attribution-NonCommercial License](https://creativecommons.org/licenses/by-nc/4.0/), which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

Rapid Advances in Mobile Mass Spectrometry Enhance Tracer Hydrology and Water Management

Andrea L. Popp^{1,2} , Cara C. M. Manning^{3,4} , and Julia L. A. Knapp⁵ 

¹Department of Geosciences, University of Oslo, Oslo, Norway, ²Department of Physical Geography, Stockholm University, Stockholm, Sweden, ³Plymouth Marine Laboratory, Plymouth, UK, ⁴National Centre for Earth Observation, Plymouth Marine Laboratory, Plymouth, UK, ⁵Department of Earth Sciences, Durham University, Durham, UK

Abstract Dissolved gases, including noble gases, are versatile environmental tracers. Historically, the application of dissolved (noble) gases as tracers in hydrology used to be limited because their measurement required expensive, laboratory-based instrumentation operated by highly trained personnel. Here, we highlight recent advances in mobile mass spectrometry (MS) methods for noble and other dissolved gases, which enable low cost, high-throughput, real-time measurements. We also present applications using mobile MS to quantify hydrological and biogeochemical processes in groundwater and surface waters and to assess hazards and risks to aquatic environments. Finally, we indicate potential future applications of these instruments to enhance hydrological research.

Plain Language Summary Measurements of hydrological tracers (i.e., specific chemicals or isotopes, whose abundance reflects the properties and history of the sampled water) are an established way to observe how water flows and how solutes might change at and below the Earth's surface over time. Dissolved gases, including noble (inert) gases such as helium, as well as reactive gases such as oxygen and nitrogen, are effective and versatile hydrological tracers. However, until recently, these measurements typically required large, expensive, laboratory-based instrumentation operated by highly trained people, which has limited the use of these tracers. Here, we highlight recent advances in instrumentation for dissolved gas measurements that can be deployed in the field and are both less expensive and easier to operate than conventional lab-based instruments. Thus, this new technology will enable more scientists to conduct dissolved gas measurements and to look at processes with a higher temporal and spatial resolution. We describe different applications where these new methods have helped to study the quantity and quality of water, as well as potential future applications of these methods.

1. Introduction

For many years, hydrologists have been applying a set of discipline-specific tracer-based approaches to assess water sources, pathways, and timescales of flow with the ultimate goal to enhance our understanding of how water moves through the environment (e.g., Cook & Herczeg, 2000; Jasechko, 2019; Sprenger et al., 2019). Surface-water and catchment hydrologists have traditionally focused on the use of stable water isotopes (e.g., Gat et al., 1996; Leibundgut et al., 2009), while groundwater hydrologists have a long tradition of using dissolved (noble) gases as tracers of subsurface water movement (e.g., Aeschbach-Hertig & Solomon, 2013; Mazor, 1972), similar to approaches in the field of tracer oceanography (Aeschbach, 2016; Hamme et al., 2017; Loose & Jenkins, 2014; Stanley et al., 2009). One of the possible reasons for this separate development in methods is that stable water isotopes are mostly suitable to track younger (surface) waters, whereas (noble) gas tracers are typically used to identify older groundwaters (e.g., Jasechko, 2019; Sprenger et al., 2019). Traditionally, both stable water isotope and noble gas measurements have required the use of expensive, laboratory-based mass spectrometry (MS) systems operated by dedicated technical personnel. However, since the mid-2000s, the development of lower-cost “plug and play” laser spectroscopy systems for the analysis of stable water isotopes has greatly expanded the number of laboratories conducting these measurements (e.g., Galewsky et al., 2016; von Freyberg et al., 2017). More recently (within the last decade), relatively low-cost commercial membrane inlet or gas equilibration MS systems have become available for noble gas analysis, from companies such as Hiden Analytical (www.hidenanalytical.com), Gasometrix (www.gasometrix.com), and Bay Instruments (www.bayinstruments.com). Over time, these commercially available systems have become increasingly user-friendly with regard to setup and data

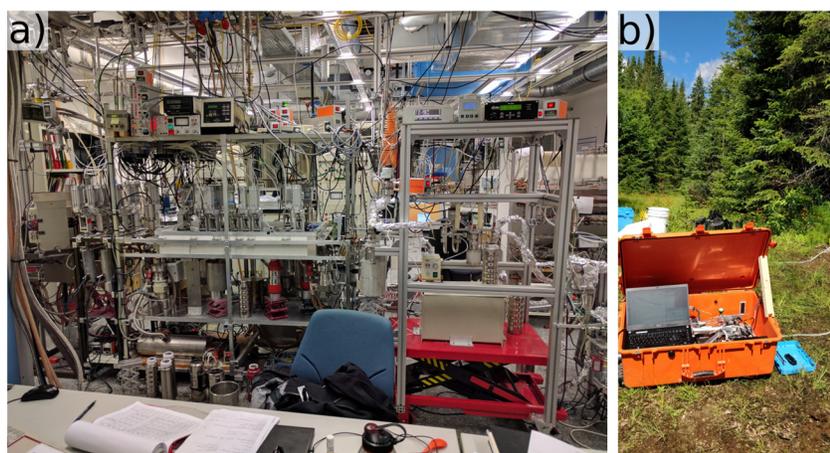


Figure 1. Examples of (a) lab-based and (b) mobile mass spectrometry for the analysis of dissolved (noble) gases.

processing, and now represent new, powerful tools to advance the field of hydrology by providing insights and perspectives from novel data sets.

In this study, we delineate recent advances in mobile MS that now render gas tracer measurements accessible to a wider range of researchers. This commentary presents new avenues in tracer hydrology by (a) highlighting latest advances in low-cost and low-maintenance mobile MS systems and (b) identifying various potential applications of mobile MS to gain new insights into hydrological systems.

1.1. Calls for New Technologies

A recently published community study (Blöschl et al., 2019) calls for “innovative technologies to measure surface and subsurface properties, states and fluxes at a range of spatial and temporal scales” to advance the field of hydrology. Likewise, Beven et al. (2020) identify the need for “new observational techniques to test process representations and gain improved understanding of hydrological processes.” Similarly, an increasing number of review papers suggest that adding more novel (tracer) data to (numerical) modeling can reduce model uncertainties (Schilling et al., 2019; Sprenger et al., 2019) and improve system understanding (Brunner et al., 2017). These calls underscore the continued need for novel measurement techniques to advance our understanding of hydrological processes. We therefore highlight recent studies using dissolved (noble) gas measurements analyzed with mobile MS to demonstrate the new scientific insights that can be gained with these systems.

1.2. Lab-Based Versus Mobile MS: Advantages and Limitations

The biggest advantage of lab-based MS systems is their analytical precision, which enables reliable measurements of isotope ratios as well as a wide range of gas species typically present at very low quantities, like neon or xenon. Conversely, the most common disadvantage of lab-based systems is the high cost associated with their acquisition, operation, and maintenance (e.g., need for a lab technician, space and supply of material; Figure 1a). Additionally, the complex procedures of sample acquisition, handling, and laboratory analysis hamper high-resolution tracer measurements, which are needed to identify hydrological dynamics and spatial patterns.

Mobile MS systems (Brennwald et al., 2016; Cassar et al., 2009; Chatton et al., 2017; Kaiser et al., 2005; Manning et al., 2016; Tortell, 2005) are comparatively inexpensive, easy to operate, and high-throughput (Figure 1b). However, the use of mobile systems does not come without its limitations including a lower analytical precision, the difficulty of transporting such systems to remote areas due to their weight (~30–50 kg), and challenges of operating the system in the field, particularly in areas lacking stable power supply. It is difficult to exactly quantify the uncertainties originating from these limitations, as there are large variations across systems in all of these aspects. For example, the level of sample purification before analysis can range

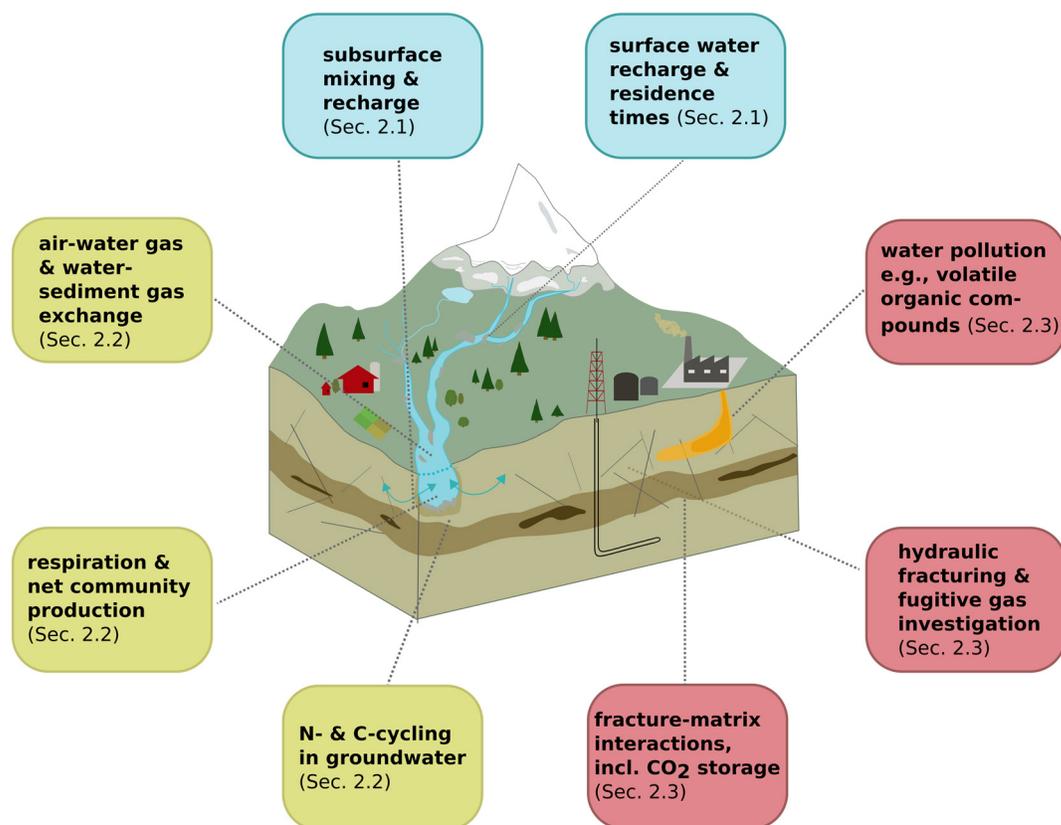


Figure 2. Fields of application of mobile mass spectrometry (MS) to improve hydrological process understanding and water resource management, including hydrological (blue) and biogeochemical (yellow) processes, as well as hazard and risk assessment (red).

from none (e.g., Brennwald et al., 2016) to relatively elaborate systems including a dry ice/isopropanol water trap, a CO₂ trap and getters (e.g., Visser et al., 2013), but sample purification of mobile systems is never as sophisticated as with the complex laboratory setups. Challenges associated with the continuous operation under variable environmental conditions are also encountered, for example, clogging of the membrane and water filters, overheating or freezing of parts of the system, and diurnal temperature cycles affecting measurements. Moreover, the relatively large amount of water needed for on-site analysis can render portable systems unsuitable for studying systems on centimeter to meter scales (e.g., streambeds), because the required pumping rate can disrupt the natural flow paths. Similarly, in some settings (e.g., wells with a low hydraulic conductivity) the required pumping rate to operate portable MS systems can also prohibit their use (Popp, 2019). Despite these drawbacks, the performance of mobile MS systems is sufficient and promising for many in-field applications (Davey et al., 2011; Popp, 2019).

2. Recent and Potential Fields of Application of Mobile MS

This section exemplifies various recent and potential applications of mobile MS systems, which have been employed to address scientific questions at the intersection of hydrology, biogeochemistry, and hazard and risk management as shown in Figure 2.

2.1. Hydrological Processes

Dissolved noble gases analyzed by mobile MS systems have successfully been used to assess groundwater flow (Moeck et al., 2017), mixing between surface water and groundwater (Popp et al., 2021; 2019), and apparent groundwater ages (Moeck et al., 2021). Further examples of potential advances using mobile MS

applications relate to groundwater recharge, particularly in mountainous regions. Here, noble gas measurements can be used to approximate recharge elevations as recently demonstrated by Doyle et al. (2015) and Peters et al. (2018) (using traditional lab-based noble gas analysis). Schilling et al. (2021) used dissolved noble gas tracers to quantify groundwater recharge dynamics from snowmelt. Their approach presents a complementary method to using stable water isotopes alone, which are prone to biases in snow-dominated catchments.

2.2. Biogeochemical Processes in Aquatic Systems

Mobile MS systems have also been applied to quantify biogeochemical dynamics in aquatic systems. Following the trend to more interdisciplinary and multidisciplinary research (e.g., Li et al., 2021), the combined analysis of noble and reactive gases can elucidate a range of catchment and groundwater processes, including reaction and physical transport processes (e.g., Chatton, 2017). Example studies of application include the assessment of greenhouse gas emissions from rivers (Vautier et al., 2020), the quantification of oxygen inputs to groundwater (Mächler et al., 2013), the estimation of denitrification dynamics in riparian aquifers (Popp et al., 2020), and the quantification of gas transfer velocity in shallow waters (Weber et al., 2019). Moreover, the measurement of natural oxygen fluctuations together with added tracers such as noble gases, propane, or other gases can be used to quantify reaeration and net community production in surface waters (Knapp et al., 2019; Manning et al., 2019).

2.3. Hazard and Risk Assessment of Hydrological Systems

The real-time monitoring enabled by mobile systems makes them highly beneficial in the context of contaminant transport and energy storage and extraction. A recent study highlighted the use of a mobile MS system during controlled hydraulic reservoir stimulation experiments (Roques et al., 2020), while Hoffmann et al. (2020) used mobile MS analysis to quantify the exchange between fracture fluid and the rock matrix. Mobile MS systems have also been applied to monitor gas transport during controlled injections into aquifers (Cahill et al., 2020; Chatton et al., 2017; Chopra, 2020; Soares, 2020). Similarly, real-time measurements of methane concentrations in groundwater can help to monitor natural gas development (Ruybal et al., 2018) and to distinguish natural from anthropogenic methane sources in groundwater (Darrah et al., 2014, 2015; used grab samples). In the field of carbon capture and storage, real-time measurements of noble gases can be used to monitor the effectiveness of carbon removal processes (Sundal et al., 2019) and serve as an early warning sign for CO₂ leakage from storage facilities, as demonstrated in laboratory experiments (Kilgallon et al., 2018). Monitoring atmospheric and aqueous contaminants (e.g., volatile and semi-volatile organic compounds) in industrial settings is another promising application of these instruments (Bell et al., 2015; Cheng et al., 2021). In many of these applications, measurements with mobile techniques can be used to monitor changes over time or identify suitable locations for the collection of discrete samples.

3. Outlook and Future Applications

Previous studies have demonstrated the large range of possible applications of mobile MS. The increasing availability of these systems, along with their simple operation and limited cost, provides numerous opportunities for their use in novel contexts to enhance our understanding of hydrological processes.

3.1. Long-Term, Unattended Monitoring Strategies in Remote Areas

Mobile MS can provide a range of future opportunities for monitoring. Systems that can operate unattended for extended periods of time (e.g., weeks to months)—maybe even transmitting their data in real time—can benefit in risk environments or whenever long-term data are required, for example, in the monitoring of organic species in nuclear waste ponds (Brkić et al., 2018). Time series measurements also allow capturing high-frequency variability that is missed by traditional methods of low-frequency grab sampling, thus providing novel insights into hydrological and biogeochemical processes (e.g., Rode et al., 2016). Likewise, mobile MS can increase our ability to record dynamic changes in less accessible locations, and MS systems

could be deployed on new platforms that are difficult to reach for regular spot measurements, like tree canopy layers or even underwater (Camilli & Duryea, 2009; Chua et al., 2016).

3.2. Combining Analysis Techniques Enhances Hydrological Process Understanding

Surface water and groundwater hydrologists have traditionally employed discipline-specific approaches and techniques to answer questions that are often very similar: Where does the water come from and how long does it take to travel through the system? What reactions may have occurred along the way, and how can we predict possible impacts on the larger system? Different tracers (analyzed with different instruments) may provide complementary insights into different processes and time scales, thus increasing our integrated understanding of hydrology and biogeochemistry if employed together. For example, helium-4 and other noble gas measurements can complement stable water isotope analysis during recharge events, resulting in an improved estimation of the groundwater age distribution or mixing processes. Further examples include, but are not limited to, combining measurements of conservative water tracers like stable water isotopes with the analysis of reactive gases like CO₂ and CH₄ (concentration and/or δ¹³C), or dissolved organic carbon, to identify biogeochemical processes or leakage along flowpaths. Coupling radon measurement devices with mobile MS systems is also a promising way to locate groundwater inputs to streams or untangle mixing and travel times of very young water (Popp et al., 2021). Combining different measurement techniques on different spatial and temporal scales further provides an opportunity to monitor and detect long-term changes and improve the integration of hydrology and biogeochemistry (e.g., Li et al., 2021; Vonk et al., 2019).

3.3. Novel Data Sets can Help to Constrain Models

Last but not least, data obtained from mobile MS can serve in the calibration and validation of hydrologic models. For many research questions, it is pivotal to measure different types of data that exhibit different physical and chemical behavior and characteristics to better constrain uncertainties of model parameters. High spatiotemporal resolution measurements with mobile MS systems could also improve models of processes that govern the exchange of gases between shallow groundwater and the atmosphere, such as ebullition and changes in soil moisture, air temperature, and barometric pressure (Freundt et al., 2013; Jones et al., 2014). Consequently, insights provided by tracer measurements from mobile MS have the potential to considerably enhance our hydrologic system understanding and thereby safeguard sustainable water use.

Data Availability Statement

No data, code, or models were generated for this article.

Acknowledgments

The authors thank two anonymous reviewers and the associate editor for their helpful feedback that improved the manuscript.

References

- Aeschbach-Hertig, W., & Solomon, D. K. (2013). Noble gas thermometry in groundwater hydrology. In P. Burnard (Ed.), *The noble gases as geochemical tracers* (pp. 81–122). Berlin: Springer. https://doi.org/10.1007/978-3-642-28836-4_5
- Aeschbach, W. (2016). New perspectives for noble gases in oceanography. *Journal of Geophysical Research: Oceans*, 121(8), 6550–6554. <https://doi.org/10.1002/2016JC012133>
- Bell, R. J., Davey, N. G., Martinsen, M., Collin-Hansen, C., Krogh, E. T., & Gill, C. G. (2015). A field-portable membrane introduction mass spectrometer for real-time quantitation and spatial mapping of atmospheric and aqueous contaminants. *Journal of the American Society for Mass Spectrometry*, 26(2), 212–223. <https://doi.org/10.1021/jasms.8b0496110.1007/s13361-014-1028-3>
- Beven, K., Asadullah, A., Bates, P., Blyth, E., Chappell, N., Child, S., et al. (2020). Developing observational methods to drive future hydrological science: Can we make a start as a community? *Hydrological Processes*, 34(3), 868–873. <https://doi.org/10.1002/hyp.13622>
- Blöschl, G., Bierkens, M. F. P., Chambel, A., Cudennec, C., Destouni, G., Fiori, A., et al. (2019). Twenty-three unsolved problems in hydrology (UPH)—A community perspective. *Hydrological Sciences Journal*, 64(10), 1141–1158. <https://doi.org/10.1080/02626667.2019.1620507>
- Brennwald, M. S., Schmidt, M., Oser, J., & Kipfer, R. (2016). A portable and autonomous mass spectrometric system for on-site environmental gas analysis. *Environmental Science & Technology*, 50(24), 13455–13463. <https://doi.org/10.1021/acs.est.6b03669>
- Brkić, B., Giannoukos, S., Taylor, S., & Lee, D. F. (2018). Mobile mass spectrometry for water quality monitoring of organic species present in nuclear waste ponds. *Analytical Methods*, 10(48), 5827–5833. <https://doi.org/10.1039/C8AY02537A>
- Brunner, P., Therrien, R., Renard, P., Simmons, C. T., & Franssen, H.-J. H. (2017). Advances in understanding river-groundwater interactions: River-groundwater interactions. *Reviews of Geophysics*, 55(3), 818–854. <https://doi.org/10.1002/2017RG000556>
- Cahill, A., Ladd, B., Chao, J., Soares, J., Cary, T., Finke, N., et al. (2020). Controlled natural gas release experiment in a confined aquifer, Northeastern British Columbia (NTS 094A/04): Activity report 2018–2019. *Geoscience BC Summary of Activities 2019*, 145–160. Retrieved from http://www.geosciencebc.com/i/pdf/SummaryofActivities2019/EW/Project/%202016-043_EW/%20SOA2019.pdf

- Camilli, R., & Duryea, A. N. (2009). Characterizing spatial and temporal variability of dissolved gases in aquatic environments with in situ mass spectrometry. *Environmental Science & Technology*, 43(13), 5014–5021. <https://doi.org/10.1021/es803717d>
- Cassar, N., Barnett, B. A., Bender, M. L., Kaiser, J., Hamme, R. C., & Tilbrook, B. (2009). Continuous high-frequency dissolved O₂/Ar measurements by equilibrator inlet mass spectrometry. *Analytical Chemistry*, 81(5), 1855–1864. <https://doi.org/10.1021/ac802300u>
- Chatton, E. (2017). *Contribution of dissolved gases to the understanding of groundwater hydrobiogeochemical dynamics* (PhD Thesis). Université Rennes 1. Retrieved from <https://tel.archives-ouvertes.fr/tel-01810743>
- Chatton, E., Labasque, T., de La Bernardie, J., Guihéneuf, N., Bour, O., & Aquilina, L. (2017). Field continuous measurement of dissolved gases with a CF-MIMS: Applications to the physics and biogeochemistry of groundwater flow. *Environmental Science & Technology*, 51(2), 846–854. <https://doi.org/10.1021/acs.est.6b03706>
- Cheng, Y., Liu, M., Zhao, B., Yang, L., Guo, C., & Zhang, L. (2021). A sandwich temperature control membrane inlet mass spectrometer for dissolved gases and volatile organic compounds in aqueous solution. *Talanta*, 221, 121464. <https://doi.org/10.1016/j.talanta.2020.121464>
- Chopra, C. (2020). *Quantification and mapping of methane emissions using eddy covariance in a controlled subsurface synthetic natural gas release experiment*. (Master's thesis). University of British Columbia. <https://doi.org/10.14288/1.0395399>
- Chua, E. J., Savidge, W., Short, R. T., Cardenas-Valencia, A. M., & Fulweiler, R. W. (2016). A review of the emerging field of underwater mass spectrometry. *Frontiers in Marine Science*, 3, 209. <https://doi.org/10.3389/fmars.2016.00209>
- Cook, P., & Herczeg, A. L. (2000). *Environmental tracers in subsurface hydrology* (Vol. 53(9)). New York, NY: Springer Science+Business Media. <https://doi.org/10.1017/CBO9781107415324.004>
- Darrah, T. H., Jackson, R. B., Vengosh, A., Warner, N. R., & Poreda, R. J. (2015). Noble gases: A new technique for fugitive gas investigation in groundwater. *Ground Water*, 53(1), 23–28.
- Darrah, T. H., Vengosh, A., Jackson, R. B., Warner, N. R., & Poreda, R. J. (2014). Noble gases identify the mechanisms of fugitive gas contamination in drinking-water wells overlying the Marcellus and Barnett Shales. *Proceedings of the National Academy of Sciences*, 111(39), 14076–14081. <https://doi.org/10.1073/pnas.1322107111>
- Davey, N. G., Krogh, E. T., & Gill, C. G. (2011). Membrane-introduction mass spectrometry (MIMS). *TRAC Trends in Analytical Chemistry*, 30(9), 1477–1485. <https://doi.org/10.1016/j.trac.2011.05.003>
- Doyle, J. M., Gleeson, T., Manning, A. H., & Mayer, K. U. (2015). Using noble gas tracers to constrain a groundwater flow model with recharge elevations: A novel approach for mountainous terrain. *Water Resources Research*, 51(10), 8094–8113. <https://doi.org/10.1002/2015WR017274>
- Freundt, F., Schneider, T., & Aeschbach-Hertig, W. (2013). Response of noble gas partial pressures in soil air to oxygen depletion. *Chemical Geology*, 339, 283–290. <https://doi.org/10.1016/j.chemgeo.2012.07.026>
- Galewsky, J., Steen-Larsen, H. C., Field, R. D., Worden, J., Risi, C., & Schneider, M. (2016). Stable isotopes in atmospheric water vapor and applications to the hydrologic cycle. *Reviews of Geophysics*, 54(4), 809–865. <https://doi.org/10.1002/2015rg000512>
- Gat, J. R., Shemesh, A., Tziperman, E., Hecht, A., Georgopoulos, D., & Basturk, O. (1996). The stable isotope composition of waters of the eastern Mediterranean Sea. *Journal of Geophysical Research*, 101(C3), 6441–6451. <https://doi.org/10.1029/95JC02829>
- Hamme, R. C., Emerson, S. R., Severinghaus, J. P., Long, M. C., & Yashayaev, I. (2017). Using noble gas measurements to derive air-sea process information and predict physical gas saturations. *Geophysical Research Letters*, 44(19), 9901–9909. <https://doi.org/10.1002/2017GL075123>
- Hoffmann, R., Goderniaux, P., Jamin, P., Chatton, E., Bernardie, J., Labasque, T., et al. (2020). Continuous dissolved gas tracing of fracture-matrix exchanges. *Geophysical Research Letters*, 47(17). e2020GL088944. <https://doi.org/10.1029/2020GL088944>
- Jasechko, S. (2019). Global isotope hydrogeology—Review. *Reviews of Geophysics*, 57(3), 835–965. <https://doi.org/10.1029/2018RG000627>
- Jones, K. L., Lindsay, M. B., Kipfer, R., & Mayer, K. U. (2014). Atmospheric noble gases as tracers of biogenic gas dynamics in a shallow unconfined aquifer. *Geochimica et Cosmochimica Acta*, 128, 144–157. <https://doi.org/10.1016/j.gca.2013.12.008>
- Kaiser, J., Reuer, M. K., Barnett, B., & Bender, M. L. (2005). Marine productivity estimates from continuous O₂/Ar ratio measurements by membrane inlet mass spectrometry. *Geophysical Research Letters*, 32(19), L1960. <https://doi.org/10.1029/2005GL023459>
- Kilgallon, R., Gilfillan, S., Edlmann, K., McDermott, C., Naylor, M., & Haszeldine, R. (2018). Experimental determination of noble gases and SF₆ as tracers of CO₂ flow through porous sandstone. *Chemical Geology*, 480, 93–104. <https://doi.org/10.1016/j.chemgeo.2017.09.022>
- Knapp, J. L., Osenbrück, K., Brennwald, M. S., & Cirpka, O. A. (2019). In-situ mass spectrometry improves the estimation of stream reaeration from gas-tracer tests. *The Science of the Total Environment*, 655, 1062–1070. <https://doi.org/10.1016/j.scitotenv.2018.11.300>
- Leibundgut, C., Maloszewski, P., & Külls, C. (2009). *Tracers in hydrology*. Chichester; Hoboken, NJ: Wiley-Blackwell. <https://doi.org/10.1002/9780470747148>
- Li, L., Sullivan, P. L., Benettin, P., Cirpka, O. A., Bishop, K., Brantley, S. L., & Kirchner, J. W. (2021). Toward catchment hydro-biogeochemical theories. *WIREs Water*, 8(1). e1495. <https://doi.org/10.1002/wat2.1495>
- Loose, B., & Jenkins, W. (2014). The five stable noble gases are sensitive unambiguous tracers of glacial meltwater. *Geophysical Research Letters*, 41(8), 2835–2841. <https://doi.org/10.1002/2013GL058804>
- Mächler, L., Peter, S., Brennwald, M. S., & Kipfer, R. (2013). Excess air formation as a mechanism for delivering oxygen to groundwater: Oxygenation of groundwater by excess air formation. *Water Resources Research*, 49(10), 6847–6856. <https://doi.org/10.1002/wrcr.20547>
- Manning, C. C., Stanley, R. H. R., & Lott, D. E. (2016). Continuous measurements of dissolved Ne, Ar, Kr, and Xe ratios with a field-deployable gas equilibration mass spectrometer. *Analytical Chemistry*, 88(6), 3040–3048. <https://doi.org/10.1021/acs.analchem.5b03102>
- Manning, C. C., Stanley, R. H. R., Nicholson, D. P., Loose, B., Lovely, A., Schlosser, P., & Hatcher, B. G. (2019). Changes in gross oxygen production, net oxygen production, and air-water gas exchange during seasonal ice melt in Whycocomagh Bay, a Canadian estuary in the Bras d'Or Lake system. *Biogeosciences*, 16(17), 3351–3376. <https://doi.org/10.5194/bg-16-3351-2019>
- Mazor, E. (1972). Paleotemperatures and other hydrological parameters deduced from noble gases dissolved in groundwaters; Jordan Rift Valley, Israel. *Geochimica et Cosmochimica Acta*, 36(12), 1321–1336. [https://doi.org/10.1016/0016-7037\(72\)90065-8](https://doi.org/10.1016/0016-7037(72)90065-8)
- Moeck, C., Popp, A. L., Brennwald, M. S., Kipfer, R., & Schirmer, M. (2021). Combined method of ³H/³He apparent age and on-site helium analysis to identify groundwater flow processes and transport of perchloroethylene (PCE) in an urban area. *Journal of Contaminant Hydrology*, 238, 103773. <https://doi.org/10.1016/j.jconhyd.2021.103773>
- Moeck, C., Radny, D., Popp, A., Brennwald, M., Stoll, S., Auckenthaler, A., et al. (2017). Science of the total environment characterization of a managed aquifer recharge system using multiple tracers. *The Science of the Total Environment*, 609, 701–714. <https://doi.org/10.1016/j.scitotenv.2017.07.211>
- Peters, E., Visser, A., Esser, B., & Moran, J. (2018). Tracers reveal recharge elevations, groundwater flow paths and travel times on Mount Shasta, California. *Water*, 10(2), 97. <https://doi.org/10.3390/w10020097>
- Popp, A. L. (2019). *Tracing surface water-groundwater interactions with in-situ noble gas analysis* (PhD Thesis). ETH Zurich. <https://doi.org/10.3929/ethz-b-000403384>

- Popp, A. L., Manning, C. C., Brennwald, M. S., & Kipfer, R. (2020). A new in situ method for tracing denitrification in riparian groundwater. *Environmental Science & Technology*, 54(3), 1562–1572. <https://doi.org/10.1021/acs.est.9b05393>
- Popp, A. L., Pardo-Alvarez, A., Schilling, O., Musy, S., Peel, M., Purtschert, R., et al. (2021). A framework for untangling transient groundwater mixing and travel times. *Water Resources Research*, 57. <https://doi.org/10.1029/2020WR028362>
- Popp, A. L., Scheidegger, A., Moeck, C., Brennwald, M. S., & Kipfer, R. (2019). Integrating Bayesian groundwater mixing modeling with on-site helium analysis to identify unknown water sources. *Water Resources Research*, 55(12), 10602–10615. <https://doi.org/10.1029/2019WR025677>
- Rode, M., Wade, A. J., Cohen, M. J., Hensley, R. T., Bowes, M. J., Kirchner, J. W., et al. (2016). Sensors in the stream: The high-frequency wave of the present. *Environmental Science & Technology*, 50(19), 10297–10307. <https://doi.org/10.1021/acs.est.6b02155>
- Roques, C., Weber, U. W., Brixel, B., Krietsch, H., Dutler, N., Brennwald, M. S., & Kipfer, R. (2020). In situ observation of helium and argon release during fluid-pressure-triggered rock deformation. *Scientific Reports*, 10(1), 6949. <https://doi.org/10.1038/s41598-020-63458-x>
- Ruybal, C. J., Wilkin, R. T., Rue, K. D., McCray, J. E., & DiGiulio, D. C. (2018). New equilibrator design for rapid detection of methane in groundwater during purging. *Environmental Engineering Science*, 35(9), 897–908. <https://doi.org/10.1089/ees.2018.0011>
- Schilling, O. S., Cook, P. G., & Brunner, P. (2019). Beyond classical observations in hydrogeology: The advantages of including exchange flux, temperature, tracer concentration, residence time, and soil moisture observations in groundwater model calibration. *Reviews of Geophysics*, 57(1), 146–182. <https://doi.org/10.1029/2018RG000619>
- Schilling, O. S., Parajuli, A., Otis, C. T., Müller, T. U., Quijano, W. A., Tremblay, Y., & Therrien, R. (2021). Quantifying groundwater recharge dynamics and unsaturated zone processes in snow-dominated catchments via on-site dissolved gas analysis. *Water Resources Research*, 57, e2020WR028479. <https://doi.org/10.1029/2020WR028479>
- Soares, J. V. (2020). *Characterization of gas migration and surface emissions through a controlled release experiment at the Hudson's Hope field research station, BC, Canada* (Master's thesis). University of British Columbia. <https://doi.org/10.14288/1.0389535>
- Sprenger, M., Stumpp, C., Weiler, M., Aeschbach, W., Allen, S. T., Benettin, P., & Werner, C. (2019). The Demographics of water: A review of water ages in the critical zone. *Reviews of Geophysics*, 57(3), 800–834. <https://doi.org/10.1029/2018RG000633>
- Stanley, R. H., Jenkins, W. J., Lott, D. E., & Doney, S. C. (2009). Noble gas constraints on air-sea gas exchange and bubble fluxes. *Journal of Geophysical Research*, 114(C11). <https://doi.org/10.1029/2009JC005396>
- Sundal, A., Weber, U., Brennwald, M., Ringrose, P., Flø, N., Johnsen, K., & Kipfer, R. (2019). *Monitoring real time, in-line variations of noble gas concentrations during CO₂ capture operations by means of a portable mass spectrometer (SSRN Scholarly paper No. ID 3366166)*. Rochester, NY: Social Science Research Network. <https://doi.org/10.2139/ssrn.3366166>
- Tortell, P. D. (2005). Dissolved gas measurements in oceanic waters made by membrane inlet mass spectrometry. *Limnology and Oceanography: Methods*, 3(1), 24–37. <https://doi.org/10.4319/lom.2005.3.24>
- Vautier, C., Abhervé, R., Labasque, T., Laverman, A. M., Guillou, A., Chatton, E., & de Dreuzy, J.-R. (2020). Mapping gas exchanges in headwater streams with membrane inlet mass spectrometry. *Journal of Hydrology*, 581, 124398. <https://doi.org/10.1016/j.jhydrol.2019.124398>
- Visser, A., Singleton, M. J., Hillegonds, D. J., Velsko, C. A., Moran, J. E., & Esser, B. K. (2013). A membrane inlet mass spectrometry system for noble gases at natural abundances in gas and water samples. *Rapid Communications in Mass Spectrometry*, 27(21), 2472–2482. <https://doi.org/10.1002/rcm.6704>
- von Freyberg, J., Studer, B., & Kirchner, J. W. (2017). A lab in the field: High-frequency analysis of water quality and stable isotopes in stream water and precipitation. *Hydrology and Earth System Sciences*, 21(3), 1721–1739. <https://doi.org/10.5194/hess-21-1721-2017>
- Vonk, J. E., Tank, S. E., & Walvoord, M. A. (2019). Integrating hydrology and biogeochemistry across frozen landscapes. *Nature Communications*, 10(1), 5377. <https://doi.org/10.1038/s41467-019-13361-5>
- Weber, U. W., Cook, P. G., Brennwald, M. S., Kipfer, R., & Stieglitz, T. C. (2019). A novel approach to quantify air-water gas exchange in shallow surface waters using high-resolution time series of dissolved atmospheric gases. *Environmental Science & Technology*, 53(3), 1463–1470. <https://doi.org/10.1021/acs.est.8b05318>