Debates, Dilemmas, and Discoveries

Debates, Dilemmas, and Discoveries (3D) offers rapid publication on compelling and timely issues. Contributions should answer the "so what?" question and should encourage readers to think, challenge them to do better science, and motivate them to excel in the ways in which they apply science to environmental assessment and management.

The feature provides a platform to:

- report on progress in field and laboratory research
- explore new or emerging research questions
- provide opinions and perspectives on a range of environmental topics
- debate issues
- spotlight management policies and practices
- share challenges and insights on biology, chemistry, ecology, engineering and sustainability

Guidelines and Submission: Manuscripts should be concise and written for a broad audience of policy makers, scientists, and business professionals. Manuscripts are limited to 1000 words and may include no more than 1 table or figure and up to 6 references. Manuscripts are subject to review and approval by the 3D Editors. Submit any questions and manuscripts directly to the 3D Editors (ieam3d@setac.org).

In a Nutshell. . .

TOPIC CATEGORY

Does the partitioning of perfluoroalkyl acids to soil depend on their chain length? By Coppola et al.

More experimental and field data are needed to develop reliable modeling tools for PFAS in soils.

SUSTAINABLE MINING

An Introduction to Forest-Smart Management in Extractive and Infrastructure Industries. By Damien Romet.

Specific guidelines for developing 'forest-smart' mining do not currently exist; however, frameworks from international organizations can be used to develop best practices pertaining to forest-smart principles. Involving stakeholders in developing the strategy can assist mining proponents in reducing indirect impacts.

DOI: 10.1002/ieam.4692

Does the partitioning of perfluoroalkyl acids to soil depend on their chain length?

Gianluca Coppola,[1] Stefano Polesello,[2]* Claudia Ferrario,[2] Massimo Peruzzo,[1] Roberto Lava,[3] and Massimo Mazzola[4]

[1]Eurolab srl, Cassola, Italy

[2]Water Research Institute, National Research Council of Italy (IRSA-CNR), Brugherio, Italy

[3]ARPAV, Laboratory Department, Regional Environmental Protection Agency of Veneto, Mestre, Italy

[4]ARPAV, Regional Environmental Protection Agency of Veneto, Vicenza, Italy

Present address: Roberto Lava, EFSA, European Food Safety Authority, Parma, Italy

DOI: 10.1002/ieam.4681

Modeling the leaching of perfluoroalkyl acids (PFAAs) from the soil, and their diffusion in groundwater requires knowledge of adsorption–desorption mechanisms and derivation of the partitioning constants for each perfluorinated substance (Li et al., 2018). There are many sources and databases of physicochemical partitioning constants (e.g., K_d, K_{ow}, and K_{oc}); however, experimental data are available for a limited set of substances, and measured values are often highly variable. Partitioning constants for soil depend on local soil conditions and implementation of a transport model, especially in groundwaters, necessarily requires the experimental derivation of adsorption (K_d^{ads}) and desorption (K_d^{des}) constants for various compounds in different soil types. However, since the standardized procedures are very time-consuming and expensive, the simplest alternative has usually been to apply data derived from widely accepted and available models, such as EPI Suite™ (US Environmental Protection Agency, 2012) or COSMOtherm (BIOVIA COSMOtherm, 2020) software packages.

We encountered this problem when we needed to model the diffusion of a set of PFAAs in a very large aquifer in Regione Veneto (Northern Italy), which was severely contaminated by decades of discharge from the MITENI Fluorochemical Factory (World Health Organization, 2017). The groundwater contamination plume, which extends over an area of 190 km^2 and a depth of more than 100 m, impacts both public waterworks and private wells. Concentrations of PFAAs in drinking waters reached up to 10 μg L^{-1} and these concentrations raised health concerns for hundreds of thousands of inhabitants. On one hand, we needed to reconstruct the past progression of the contamination, while

* Address correspondence to stefano.polesello@irsa.cnr.it
Published on wileyonlinelibrary.com/journal/ieam.

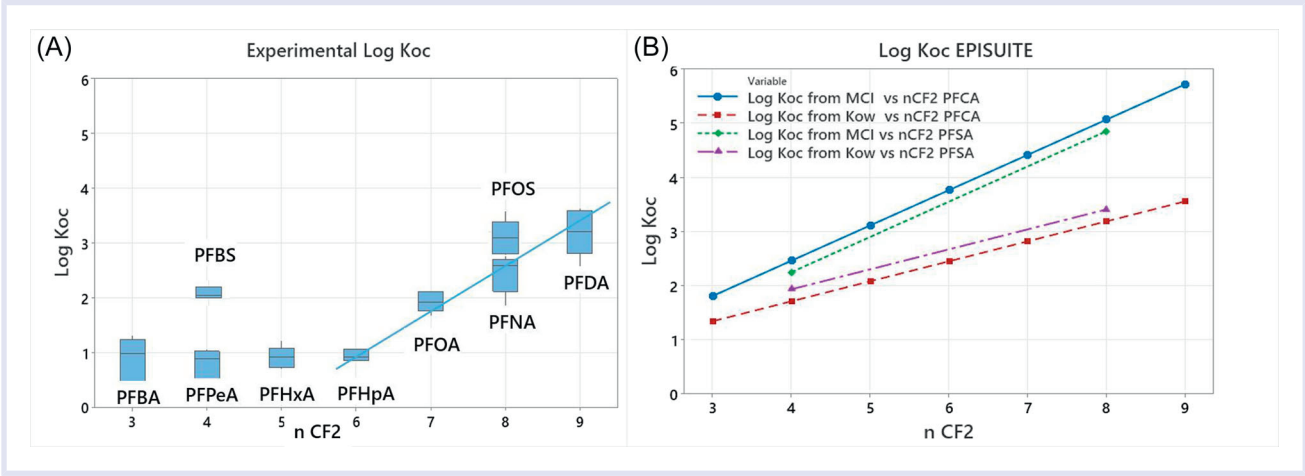

FIGURE 1 (A) Box plots of experimentally determined log K_{oc} for perfluoroalkyl acids (PFAAs); (B) regression lines between the number of CF_2 groups and log K_{oc} derived by the EPI Suite™ model

on the other hand, we wanted to forecast future progression in the three-dimensional (3D) aquifer model in order to test the effectiveness of the remediation strategies.

In this study, the liquid-solid partitioning coefficients for selected PFAAs were experimentally determined for five soil samples, which were collected by coring in 2020 at different depths (from 15 to 30m) in the saturated zone of two different sites (Vicenza and Tezze di Arzignano, VI, Italy) located at the edge of the contaminated areas. Environmental PFAA concentrations were determined in soils before the partitioning tests and were all below the detection limits (0.05 ng g^{-1}). The soil types were characterized by different organic carbon content (from 5.2% to 7.3%) and different textures in terms of silt, sand, and clay percentages. The lithological and geochemical representativeness of the studied soils was verified by comparison with reference soils cored in a nearby highly impacted area (Montecchio Maggiore, VI) which, however, were not used for sorption experiments.

The sorption experiments were conducted by a batch equilibrium method according to the Organization for Economic Co-operation and Development (OECD) 106 guideline (OECD, 2000). We obtained a set of K_ds typical of each soil, which was also converted to K_{oc} on the basis of the organic fractions of the analyzed soils. Detailed procedures and results are presented in a published report (Coppola et al., 2022). The range of K_ds and K_{oc}s of the most common PFAAs is comparable to the available literature (e.g., Nguyen et al., 2020).

We plotted the median of the K_{oc} data versus the chain length, expressed as the number of CF_2 moieties (Figure 1A). We observed that, for perfluoroalkylcarboxylates (PFCA), K_{oc}s are independent from the chain length until six CF_2, while for higher numbers of CF_2 groups, K_{oc} is linearly correlated (K_{oc} [PFCA ≥ 6] = −3.5 + 0.75[nCF_2]; p = 0.007). We analyzed only two perfluoroalkylsulfonates (PFSA; i.e., perfluorobutane sulfonic acid [PFBS] and perfluorooctane sulfonic acid [PFOS]) and the K_{oc}s are systematically higher than the corresponding PFCA with the same numbers of CF_2. The independence of K_{oc} from the number of CF_2 groups for short chain PFAAs (and on the consequence from their hydrophobicity) is confirmed by Li et al. (2018), who reported that the regression analyses between PFAS K_d with less than six CF_2 and the organic carbon (OC) of the soil are statistically not significant. The plotting of K_d constants versus the chromatographic retention times (RT) on a C18 column, used as a proxy for the hydrophobic partition mechanism (Nguyen et al., 2020), generated a trend similar to that shown in Figure 1A: in the case of short-chain PFAAs (≤C5) and novel PFASs, such as the perfluoroalkylethers ADONA and GenX, RTs were not related to Kd values, suggesting their high mobility in soil; conversely for long-chain PFCAs and PFSAs the significant linear correlation between RT and their mean K_d confirmed that hydrophobicity is the predominant driving force controlling sorption.

Despite this experimental evidence, all the tested models used to derive partition constants for PFAAs are based on a linear regression between the partition constants (i.e., K_{ow}, K_{oc}, or K_d) and the number of CF_2 units. This approach is based on the pioneering work of Higgins and Luthy (2006) on PFAA sorption on sediment, which indicated an average contribution of 0.50–0.60 log units to the measured distribution coefficients for each CF_2 moiety and an additional 0.23 log units for the sulfonates to the corresponding carboxylates. As an example, in Figure 1B we plot the K_{oc} estimated by the EPI Suite™ model using both the Molecular Connectivity Index (MCI) and a log K_{ow}-based method. The linear regression equation for the MCI method (log K_{oc} [PFCA] from MCI = −0.14 + 0.65[nCF_2]) leads to overestimated K_{oc} values up to 6 for PFDA, while lower log K_{oc} values are obtained by linear regression of K_{ow} data (log K_{oc} [PFCA] from K_{ow} = 0.23 + 0.37[nCF_2]).

It should be emphasized that the regressions for PFSA are very close and parallel to those for PFCA, and, in the case of

the MCI model, PFSA K_{oc} values lower than the corresponding PFCA values are even generated by the regression. Similar linear regressions for deriving K_{ow} were adopted by the COSMOtherm model. A recent comparative assessment of estimation methods of PFAS properties concluded that the EPI Suite™ model does not generally provide accurate estimates for PFAS (Lampic & Parnis, 2020). The same work concludes that it is unlikely that estimates of log K_{oc} for PFAS by COSMOtherm quantitative structure–property relationships are reliable because the training set includes minimally fluorinated compounds, and there is no highly fluorinated compounds representative of the PFAS family.

One possible reason for the discrepancies between experimental data on soil and outputs of partitioning models is that the latter has been developed starting from data collected on sediment, which is a more homogeneous matrix than soil in terms of composition and sorption mechanisms. Multiple factors, including the less explored role of unsaturated micropores, should be considered to interpret the fate of PFAS in soil and groundwater. Further, more experimental and field data are needed to develop reliable modeling tools that can also work for novel PFAS.

ACKNOWLEDGMENT

This work was co-funded through the LIFE Programme of the European Union (Grant Agreement number LIFE16 ENV/IT/000488—Project LIFE PHOENIX).

AUTHOR CONTRIBUTION

Gianluca Coppola: Data curation; Investigation; Methodology; Validation; Writing—review & editing. **Stefano Polesello:** Conceptualization; Data curation; Methodology; Writing—original draft; Writing—review & editing. **Claudia Ferrario:** Investigation; Methodology; Writing— review & editing. **Massimo Peruzzo:** Conceptualization; Funding acquisition; Project administration; Supervision. **Roberto Lava:** Conceptualization; Funding acquisition; Investigation; Writing—review & editing. **Massimo Mazzola:** Conceptualization; Data curation; Funding acquisition; Investigation; Methodology; Resources; Validation; Writing—original draft; Writing—review & editing.

REFERENCES

BIOVIA COSMOtherm. (2020). *Dassault Systèmes*, Release 2020. https://www.3ds.com/products-services/biovia/products/molecular-modelingsimulation/ solvation-chemistry/biovia-cosmotherm

Coppola, G., Peruzzo, M., Mazzola, M., Lava, R., Polesello, S., & Ferrario, C. (2022). Determinazione sperimentale dei coefficienti di ripartizione liquido/ solido (K_d) di sostanze perfluoroalchiliche (PFAS) su campioni di terreno. *Notiziario dei Metodi Analitici*, *2022*(2), 9–16.

Higgins, C. P., & Luthy, R. G. (2006). Sorption of perfluorinated surfactants on sediments. *Environmental Science and Technology*, *40*, 7251–7256. https://doi.org/10.1021/es061000n

Lampic, A., & Parnis, J. M. (2020). Property estimation of per- and polyfluoroalkyl substances: A comparative assessment of estimation methods. *Environmental Toxicology and Chemistry, 39*, 775–786. https://doi.org/ 10.1002/etc.4681

Li, Y. S., Oliver, D. P., & Kookana, R. S. (2018). A critical analysis of published data to discern the role of soil and sediment properties in determining sorption of per and polyfluoroalkyl substances (PFASs). *Science of the Total Environment, 628–629*, 110–120. https://doi.org/10.1016/j.scitotenv.2018.01.167

Nguyen, T. M. H., Bräunig, J., Thompson, K., Thompson, J., Kabiri, S., Navarro, D. A., Kookana, R. S., Grimison, C., Barnes, C. M., Higgins, C. P., McLaughlin, M. J., & Mueller, J. F. (2020). Influences of chemical properties, soil properties, and solution pH on soil-water partitioning coefficients of per- and polyfluoroalkyl substances (PFASs). *Environmental Science and Technology, 54*, 15883–15892. https://doi.org/10.1021/acs.est.0c05705

Organization for Economic Co-operation and Development (OECD). (2000). *Test no. 106: Adsorption-desorption using a batch equilibrium method, OECD Guidelines for the testing of chemicals, Section 1*. OECD Publishing.

US Environmental Protection Agency. (2012). *Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.11*. https://www.epa.gov/tscascreening- tools/epi-suitetm-estimation-program-interface

World Health Organization. (2017). *Keeping our water clean: The case of water contamination in the Veneto Region, Italy*. World Health Organization Regional Office for Europe. https://www.euro.who.int/__data/ assets/pdf_file/0019/341074/pfas-report-20170606-h1330-print-isbn.pdf

An introduction to forest-smart management in extractive and infrastructure industries

Damien Romet*
Embellie Advisory, Doha, Qatar
DOI: 10.1002/ieam.4682

Developed economies are increasingly recognizing the responsibility of private companies in addressing the negative impact their activities generate, and their role in tackling the challenges our societies are facing. The mining industry is no exception, and as part of their corporate social responsibility, mining companies must develop coherent environmental and social governance strategies, with a particular focus on creating sustainable local development and protecting the environment in their areas of influence.

Mining activities have a significant impact on the environment, in particular on water, forests, and biodiversity. Mines in high-income, developed countries must usually follow strict regulations regarding the environment and biodiversity. However, over half of the world's mines in forested areas are in developing countries (Maddox et al., 2019), where environmental legislation is usually less stringent, and loosely enforced. Further data collected by the World Bank show over 77% of mines are located within

* Address correspondence to damien.romet@embellieadvisory.me
Published on wileyonlinelibrary.com/journal/ieam.