

Environmental Policy & Regulation

Mobility in the context of exposure-based assessment of chemicals for drinking water resource protection

Sascha Pawlowski,^{1,*} Lothar Aicher,² Albert Berends,³ Pippa Curtis-Jackson,⁴ Andreas Häner,⁵ Juliane Hollender,^{6,7} Bernhard Jene,⁸ Karen Jenner,⁹ Aaron Redman,¹⁰ Gordon Sanders,¹¹ Nathalie Vallotton,¹² Neil Wang,¹³ and James R. Wheeler¹⁴

¹BASF SE, Ludwigshafen am Rhein, Germany

²Swiss Centre for Applied Human Toxicology (SCAHT), Basel, Switzerland

³Solvay S.A., Brussels, Belgium

⁴Environment Agency, Wallingford, UK

⁵F. Hoffmann-La Roche Ltd, Basel, Switzerland

⁶Swiss Federal Institute of Aquatic Science and Technology, Eawag, Dübendorf, Switzerland

⁷Institute of Biogeochemistry and Pollutant Dynamics, ETH Zürich, Zürich, Switzerland

⁸BASF SE, Limburgerhof, Germany

⁹Givaudan UK Ltd, Ashford, UK

¹⁰ExxonMobil Biomedical Sciences Inc., Annandale, New Jersey, USA

¹¹Givaudan International S.A., Vernier, Switzerland

¹²Dow Europe GmbH, Horgen, Switzerland

¹³Solvay S.A., Aubervilliers, France

¹⁴Corteva Agriscience, Bergen op Zoom, The Netherlands

Abstract

In order to protect European Union (EU) drinking water resources from chemical contamination, criteria for identifying persistent, mobile, and toxic (PMT) chemicals and very persistent and very mobile (vPvM) chemicals under the EU REACH Regulation were proposed by the German Environment Agency (Umweltbundesamt—UBA). Additionally, new hazard classes for PMT and vPvM substances in the revised EU classification, labeling, and packaging (CLP Regulation) are intended. Therefore, a reliable approach in the identification of potential drinking water resource contaminants is needed. The scientific basis of the property-based PMT/vPvM criteria, focusing on mobility, which dictates the migration of chemical drinking water sources, was evaluated, and a critical analysis of the deviation of sorption metrics from simple behavior was carried out. Based on our evaluation, a K_{oc} may be used for nonionic substances on a screening level only, requiring a higher tier assessment. It is considered inappropriate for hydrophilic and ionizable chemicals, particularly for soils with low organic carbon contents. The nonextractable residue formation is complex and not well understood but remains significant in limiting the mobility of chemicals through soils and sediments. In order to inform the EU commission's work on the introduction of new hazard classes for PMT and vPvM substances into the European legislation, the derivation of a tiered approach is proposed, which utilizes the weight of evidence available, with adoption of appropriate higher tier models commensurate with the nature of the substance and the data available. *Integr Environ Assess Manag* 2022;00:1–17. © 2022 The Authors. *Integrated Environmental Assessment and Management* published by Wiley Periodicals LLC on behalf of Society of Environmental Toxicology & Chemistry (SETAC).

KEYWORDS: Exposure; groundwater; mobility; nonextractable residues; persistence

INTRODUCTION

Water is a precious resource and, without it, life on earth would simply not be possible. In Europe, drinking water quality is among the highest in the world (Wendling et al., 2020; World Health Organization [WHO], 2019). The quality

of water has always been considered a matter of high priority, but recently awareness has been building over the availability of good-quality freshwater. Clearly, the continued supply of sufficient, good-quality freshwater that is fit for consumption is of major importance and concern for all. The protection of hydrological systems and maintaining them to high environmental standards is another major priority.

Annual usage of freshwater within Europe (Member and non-Member States) is approximately 140 billion m³ (EC, 2020a). It is estimated that the total volume of freshwater supplied as drinking water in the European Union (EU) is around 40 billion m³ per annum. The remaining (approx.

This article contains online-only Supporting Information.

* Address correspondence to sascha.pawlowski@basf.com

Published 25 October 2022 on wileyonlinelibrary.com/journal/ieam.

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

100 billion m³ per annum) abstracted freshwater is predominantly used for energy production (cooling water), which is entirely sourced from surface water, and for agriculture irrigation, which uses both groundwater and surface water sources (EC, 2020a). The contribution of drinking water originating from groundwater and surface water sources is approximately equivalent, although there are broad differences among Member States (EurEau, 2017).

In line with the objective of maintaining the quality of surface water, wastewater treatment plants (WWTPs), and their performance, are key in the purification of wastewater prior to the emission of effluent water into the environment. Approximately 90% of households in the EU are connected to a wastewater collection and treatment system (EurEau, 2017) and industrial chemical plants either have their own wastewater treatment facility or are connected to a municipal plant.

Besides the treatment of water, WWTPs generate significant quantities of biosolids (EC, 2020a). The disposal of sewage sludge depends upon national policy requirements and differs markedly from one country to another. According to EUROSTAT figures (statistical office of the EU; EC, 2020a), in 2016, approximately 40% of the 5.5 million tonnes of biosolids sent for disposal were incinerated and about 30% applied to agricultural land. The remaining 30% of sewage sludge underwent landfill disposal and composting. The Netherlands and Switzerland do not perform any applications of biosolids to agricultural land, whereas the majority of sewage sludge production in Ireland is applied as a natural fertilizer to farmland. Application of sewage sludge to agricultural land can result in terrestrial contamination (e.g., Harrison et al., 2006), especially if poorly degradable chemicals are released from the sludge once the biosolids themselves have been degraded. This exposure route is, therefore, considered an important scenario in the current evaluation for soil surface to groundwater leaching potential (ECETOC, 2021; European Chemical Agency [ECHA], 2016). Furthermore, some chemicals are introduced directly to the environment, for example, plant protection products applied directly on soil, which is routinely evaluated in the EU (EC, 2009).

In order to protect EU drinking water sources from chemical contamination, the German Environment Agency (Umweltbundesamt—UBA) proposed criteria for identifying persistent, mobile, and toxic (PMT) chemicals and very persistent and very mobile (vPvM) chemicals (Neumann & Schliebner, 2019) under the EU REACH Regulation (EC, 2006). Such chemicals are considered by Neumann and Schliebner (2019) to pose a hazard to the sources of drinking water. This is based on the assumption that the combination of persistence (P/vP) and mobility (M/vM) determines the ability of a chemical to reach drinking water sources and, when combined with toxicity (T), poses a potential risk to human health.

On October 14, 2020, the European Commission adopted its Chemicals Strategy for Sustainability (EC, 2020b). This strategy is part of the EU's zero pollution ambition, a key commitment of the European Green Deal, which aims to better protect citizens and the environment from harmful

chemicals and boosts innovation by promoting the use of safer and more sustainable chemicals.

In accordance with the Chemicals Strategy for Sustainability, the Commission will propose changes to the EU CLP Regulation (Regulation (EC) No 1272/2008; EC, 2008). The strategy foresees that hazard classes should be developed for PMT chemicals and for vPvM chemicals. ECHA has formally been requested to support the planned revision and development of new hazard criteria under the CLP Regulation (EC, 2021a).

This article examines the available scientific knowledge and explores options to further improve the protection of sources of drinking water. This includes an evaluation of the mobility criteria suggested as part of the PMT/vPvM criteria proposed by Neumann and Schliebner (2019), a proposed tiered approach for assessing mobility and a consideration of whether higher tier approaches (e.g., exposure or risk-based approaches) would be appropriate for the protection goal of safe drinking water sources, and proposes avenues of research and development necessary to improve comprehension of related processes.

CRITERIA FOR IDENTIFYING PMT CHEMICALS AND vPvB CHEMICALS

In the proposal by the German Environmental Agency (UBA) (Neumann & Schliebner, 2019), P and vP are assessed following the P/vP criteria as defined in Annex XIII of the REACH Regulation ("Criteria for identification of PBT/vPvB chemicals"; ECHA, 2017). Newly proposed mobility (M and vM) criteria to identify P/vP chemicals likely to contaminate water sources far from their emission point are based on the organic carbon (OC) normalized adsorption coefficient K_{oc} (L/kg). The UBA proposal for toxicity (T) describes additional criteria, beyond those already established by the PBT/vPvB assessment under the REACH Regulation (EC, 2006). Comment on these additional toxicity proposals is beyond the scope of this work. However, the authors of this article believe the additional toxicity proposals require further discussion and justification in order to determine if they are necessary to increase the protection of human health via drinking water resources.

MOBILITY CRITERIA

Mobile and very mobile (M and vM) criteria based on the log K_{oc} have been proposed by UBA to identify chemicals likely to contaminate water sources through movement between environmental compartments. Where log K_{oc} data are not available, screening assessments based on log D_{ow} (n-octanol/water distribution coefficient at pH 7.4) or log K_{ow} (n-octanol/water partition coefficient) values are proposed by UBA. Mobility classes based on Arp and Hale (2019) are summarized in Supporting Information: Table S1. Other classification criteria in soil have been in existence for some time for pesticides (generally nonpolar pesticides in agricultural soils) and were also based on K_{oc} . McCall's classification scheme (McCall et al., 1981; Supporting Information: Table S2) has been the most frequently used soil

mobility classification scheme. The FAO (Food & Agriculture Organization) has also developed its own soil mobility classification criteria for pesticides (Supporting Information: Table S3), again based on K_{oc} , and they are recommended for use by the United States Environmental Protection Agency (USEPA) (Food & Agriculture Organization of the United Nations [FAO], 2000).

These mobility classification scheme classes are somewhat arbitrary, but they cover a large range of mobility classes, expressed as K_{oc} or $\log K_{oc}$. While a frequently adopted approach, this metric will be examined and discussed in detail later in this article.

REVIEW OF MONITORING DATA AND EVALUATION OF PROPOSED P/vP AND M/vM CRITERIA

The PMT/vPvM classification proposed by UBA (Neumann & Schliebner, 2019) was developed for application to REACH registered chemicals, which typically represents the class of industrial chemicals excluding other chemicals such as pharmaceutical and agrochemical active ingredients or food and feed additives. Recently, the European Commission has proposed changes to the CLP Regulation to develop hazard classes for PMT chemicals and for vPvM chemicals (EC, 2020b). Within the UBA proposed PMT/vPvM classification, constituents and transformation/degradation products are considered relevant for the assessment if they exceed 0.1% weight by weight (w/w) (Neumann & Schliebner, 2019) and this is aligned with REACH PBT/vPvB assessment guidance (ECHA, 2017).

Measured monitoring data of a large number of candidate chemicals under the EU Water Framework Directive revealed measured environmental concentrations ranging from 0.00001 to 2.7 $\mu\text{g/L}$, 0.0005 to 12.5 $\mu\text{g/L}$, and 0.0005 to 20 $\mu\text{g/L}$ for the median, 90th, and 95th percentile, respectively (Carvalho et al., 2016). Consequently, taking the 0.1% (w/w) constituent threshold into account, the majority of the expected metabolite concentrations would be ≤ 0.1 ng/L. For many chemicals, an adequate analytical method is

not available, which allows for both sample concentration and analytical measurement of such low concentrations.

Both the EU and the US plant protection regulations consider 10% of the applied parent (or 5% if technically feasible) as a common limit for metabolite identification and risk assessment. Identification and quantification at levels below this limit are practically very difficult. Also, the European Medical Agency (EMA) guidance for environmental risk assessment of pharmaceuticals allows for an evaluation of the risks of metabolites that are $\geq 10\%$ of the administered dose if a total residue approach suggests a potential risk (European Medicines Agency [EMA], 2006).

Regulation EC 1107/2009 (EC, 2009) sets the analytical reporting threshold of 0.1 $\mu\text{g/L}$ for some pesticides and their metabolites in drinking water. While challenging for some chemicals, this seems to be a widely accepted limit for routine analysis of drinking water samples.

Analytical monitoring data in surface and groundwater were used in the justification of the PMT concept proposed by UBA (Neumann & Schliebner, 2019). The European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) (2021) has used many of the same monitoring data, combined with some more recently published data, to evaluate the relationship between P (persistent) and M (mobile) criteria and the observed measured concentrations in surface and groundwater.

The UK Environment Agency (EA) conducts monitoring of surface and groundwater, maintaining a database of the concentrations of detected substances (EA, 2019). Data from this source, classified as “Freshwater—Rivers,” “Groundwater—Pit,” “Groundwater—Borehole,” and “Groundwater—Spring,” were analyzed by ECETOC (2021). The compiled data included the monitoring of 62 unique chemicals for which a total of 5600 analytical points (detects and nondetects) had been determined in both surface and groundwater at various locations. These monitoring data were compared with the proposed M criteria (K_{oc} , D_{ow} , or K_{ow}). The P criteria were either measured biodegradability data (e.g., ready biodegradation test) or in silico (Biowin v4.0) predicted biodegradation classification (USEPA, 2012). The results (Figures 1 and 2) show

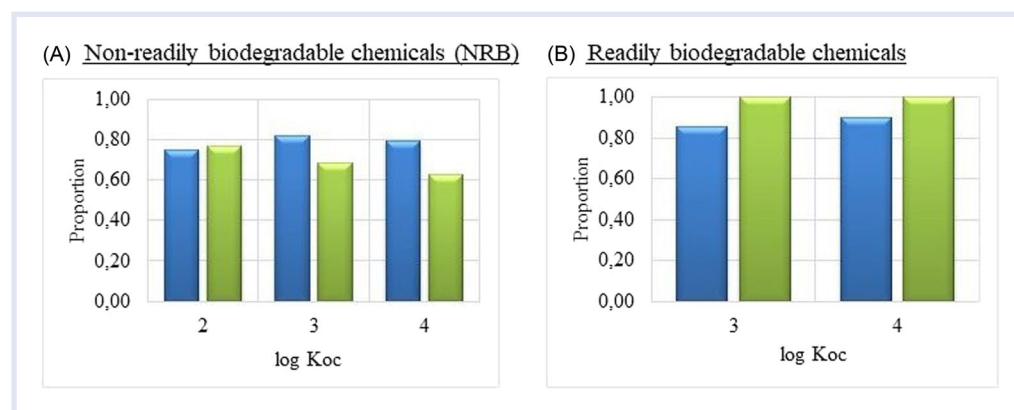


FIGURE 1 Groundwater samples detected above 0.1 $\mu\text{g/L}$ (please refer to ECETOC, 2021 for information on source data) indicates the proportion of nonreadily biodegradable (A) and readily biodegradable (B) chemicals with $\log K_{oc} \leq x$ (blue) or $\log K_{oc} > x$ (green) that exceeded 0.1 $\mu\text{g/L}$ in groundwater on at least one occasion. Reproduced with permission from ECETOC (2021)

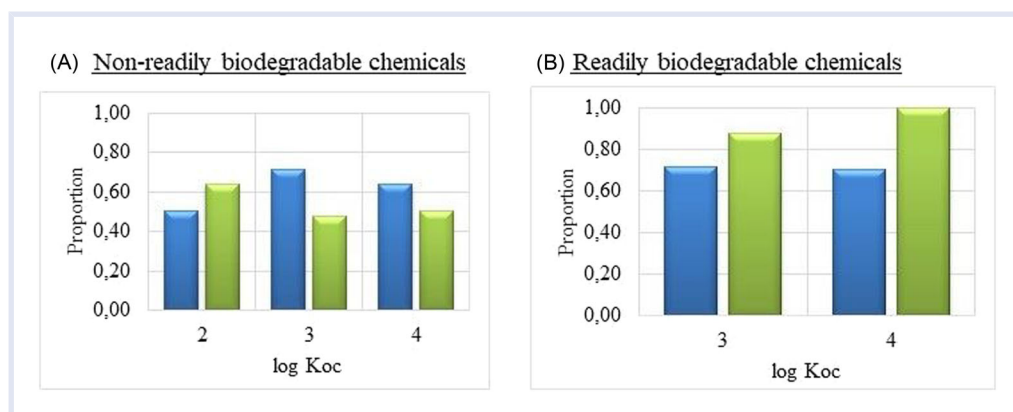


FIGURE 2 Surface water samples detected above 0.1 µg/L (please refer to ECETOC, 2021 for information on source data) indicates the proportion of nonreadily biodegradable (A) and readily biodegradable (B) chemicals with $\log K_{oc} \leq x$ (blue) or $\log K_{oc} > x$ (green) that exceeded 0.1 µg/L in surface water on at least one occasion. Reproduced with permission from ECETOC (2021)

that detected chemicals were independent of persistence and K_{oc} (ECETOC, 2021). This suggests that these oversimplistic metrics cannot serve to identify the chemicals that are likely to contaminate drinking water sources and highlights the importance of understanding local emission patterns and other factors that may influence local fate processes.

REVIEW OF M/vM METRICS

The K_{oc} , D_{ow} , or K_{ow} metrics are surrogates for expressing the sorption of a chemical to a given solid and its migration relative to the flow of water, with retardation being inversely related to mobility (Green & Karickhoff, 1990; Karickhoff et al., 1979). While the solid phase in the environment may relate to different compartments, for example, soil, subsurface soil, sediment, or biosolids in sewage treatment plants, the principles are similar, so this article refers to soil but infers other such compartments. The mobility classes mentioned above may be convenient for a preliminary level of screening, but not for a definitive regulatory classification, due to the complexity of the processes involved.

D_{ow} and K_{ow} metrics

The pH-dependent n-octanol/water distribution coefficient (D_{ow}) is proposed by UBA as the main screening criterion for mobility (Neumann & Schliebner, 2019). D_{ow} is equal to C_o/C_w , where C_o (mg/L) is the total concentration of the chemical in n-octanol and C_w (mg/L) the corresponding concentration in water (summing both ionized and nonionized forms, if applicable), when the two phases are in equilibrium.

D_{ow} values are not comparable with K_{oc} values for ionizable chemicals. According to Sigmund et al. (2022), D_{ow} values should only be used when they arguably show that the ionizable substance is not mobile. They should not be used as screening for mobile chemicals because of the “substantial uncertainty in D_{ow} extrapolation.” In addition, n-octanol has generally been used as a surrogate for lipids when screening for the potential bioaccumulation of chemicals into biota, but it should not be used as a surrogate for organic matter since n-octanol does not account for the potentially important properties of soil or sediment.

REACH registrants are required to provide K_{ow} data and ionizable chemical values for both the neutral and dissociated forms of their chemical are required. D_{ow} values can be predicted from pK_a and K_{ow} ; however, if both pK_a and K_{ow} values are predicted, the uncertainty in the predicted D_{ow} values will be magnified. Thus, if D_{ow} is used for initial screening purposes, it should ideally be measured directly experimentally or based on measured K_{ow} and pK_a .

Sorption metrics (K_d and K_{oc})

The use of the K_{oc} model for assessing soil sorption is broadly accepted for nonpolar substances and it can be considered substance-specific but soil-independent. However, this is a simplified metric and despite its convenience should still be treated with caution and only used as an approximation. The main limitations of using K_{oc} to describe mobility are discussed below.

The most relevant parameter for expressing the binding strength of a chemical to soil is the water-to-soil distribution coefficient at a given temperature (K_d ; L/kg). Two different formulations of this parameter are commonly used: the linear sorption isotherm and the nonlinear, concentration-dependent, Freundlich isotherm where the K_d value becomes a Freundlich factor (K_f) value and the Freundlich exponent ($1/n$) describes the degree of nonlinearity. Several methods have been published, which describe the experimental determination, data handling, and discussion of these approaches (e.g., Beltman et al., 2008; Doucette, 2000; EC, 2014; Green & Karickhoff, 1990; OECD Test Guidelines 106 and 121 [Organisation for Economic Cooperation and Development [OECD], 2000, 2001; Office of Prevention, Pesticides and Toxic Chemicals [OPPTS] guidance [USEPA, 2020]).

K_d is both soil and chemical specific and can therefore be used to compare the relative mobility of different chemicals in similar soils. In order to achieve a “comparative” value across different soil types, K_d is “normalized” by the OC present in the solid phase (f_{oc} , kg/kg). This gives a new partition coefficient, the OC normalized adsorption coefficient K_{oc} (L/kg), which is considered to be an intrinsic

property of nonpolar organic chemicals being sorbed and hence independent of soil type (Green & Karickhoff, 1990; Jarvis, 2016; Karickhoff et al., 1979; von Oepen et al., 1991; Wauchope et al., 2002).

The OECD 106 Test Guideline (OECD, 2000) aims to estimate the adsorption-desorption behavior of a chemical for different soil types. The goal is to obtain a sorption value, which can be used to predict partitioning under a variety of environmental conditions; to this end, equilibrium adsorption coefficients for a chemical on various soils are determined as a function of soil characteristics.

The guideline states that soil parameters of relevance to adsorption are:

- OC content;
- clay content and soil texture;
- pH (for ionizable compounds);
- the effective cation exchange capacity (CEC);
- the content of amorphous iron and aluminum oxides (particularly for volcanic and tropical soils);
- the specific surface area.

However, regulatory and modeling demands for an OC normalized value (K_{oc}) means that only this normalization value is usually reported and the influence of other soil properties is not normally considered.

Indirect K_{oc} estimation methods include the OECD 121 test guideline (OECD, 2001), which uses high-performance liquid chromatography (HPLC) for the estimation of the adsorption coefficient, K_{oc} , in soils and sewage sludge. It is based on the retention time of the substance on a specific HPLC column under specific chromatographic conditions. The measured retention time is compared to the retention times of substances with known K_{oc} values using the same HPLC conditions. The method has been validated with nonpolar reference substances, with log K_{oc} values ranging from 1.5 to 5.0. The method is not applicable to all substances, particularly where the chemical may react with the eluent or the stationary phase. The method may not work for surface-active substances, inorganic compounds, and moderate or strong organic acids and bases. For ionizable substances, two tests should be performed with both ionized and nonionized forms in an appropriate buffer. Also, care has to be taken to avoid precipitation of buffer components or test substances.

In the OECD 106 adsorption-desorption test, the test is performed in a 0.01 M solution of calcium chloride (CaCl_2) in distilled or deionized water. The 0.01 M CaCl_2 solution is used as the aqueous phase to improve centrifugation and minimize cation exchange. Therefore, for ionizable chemicals, 0.01 M CaCl_2 will block cation exchange and other ionic partitioning and may suggest (erroneously) that OC partitioning is the principal partitioning mechanism and these K_{oc} determinations will therefore be inaccurate. When considering the prominence of K_{oc} for mobility screening schemes and exposure modeling, this constraint of the methodology must be considered, particularly for ionizable chemicals.

The use of the K_{oc} model for assessing soil sorption is broadly accepted for nonpolar chemicals and K_{oc} can be considered chemical-specific but soil-independent. However, this is a simplified approach for modeling and despite its convenience should be treated with caution and only used as an approximation. A review by Wauchope et al. (2002) notes that “The temptation to regard K_{oc} as a universal constant has been strong in spite of much accumulated evidence that it is not.” Other authors have voiced similar criticisms (Jarvis, 2016; von Oepen et al., 1991). It should be recognized that soils are complex, and the issue of mobility is also complex. Therefore, a chemical's mobility in the environment cannot be adequately described by a simple K_{oc} , D_{ow} , or K_{ow} value.

DEVIATIONS OF SORPTION METRICS FROM SIMPLE BEHAVIOR

The K_{oc} model is most appropriate for describing the sorption of neutral (nonpolar) chemicals to surface soil layers with relatively high OC contents, but the approach is not applicable when interactions of chemicals with the mineral components of soils occur. These interactions become increasingly significant as the OC content of a soil decreases (Delle Site, 2001; Koskinen & Harper, 1990; Li et al., 2018). Due to degradation and dispersion/diffusion, environmentally relevant concentrations in subsurface soils and aquifers are mostly below the concentrations used in laboratory adsorption studies (Mylevaganam & Ray, 2016; Schulze-Makuch, 2011). Consequently, the environmentally relevant sorption is often underestimated by these laboratory tests, which are conducted at artificially high chemical concentrations.

Polar and ionizable chemicals

For polar and ionizable chemicals, the K_{oc} model is even more unreliable, particularly (but not exclusively) for soils with low OC contents. The coefficient of variation of K_{oc} for any given chemical has been stated to be typically in the range of 40%–60%, and the difference between the reported minimum and maximum values may be as great as an order of magnitude (Jarvis, 2016; Wauchope et al., 2002). Ionic or ionizable chemicals make up a significant proportion of registered chemicals in the EU. A statistical evaluation from 2010 showed that approximately half of the chemicals registered under the REACH regulation are ionizable compounds at environmental pH (4–9), (Arp & Hale, 2019; Franco et al., 2010). Similar findings have been published for pharmaceuticals, where 64% of a set of contemporary drugs contained an ionizable group (Manallack, 2009).

pH dependence

Changes in pH generally have little impact on the sorption of neutral, nonpolar chemicals. However, many chemicals in commerce have acid or basic functions that are partially or totally ionized at environmentally relevant pH values (Franco et al., 2010; Manallack, 2009). For these ionizable chemicals, changes in pH affect not only the speciation of the

chemical but also the nature of the soil or sediment sorption sites. Depending on the values of the acid dissociation constants (expressed as pK_a) relative to the ambient soil and water pH, the apparent K_d (or K_{oc}) may be sensitive to variations in pH.

Influence of mineral components

The clay component of soil includes minerals containing alumina and silica, which have a net negative surface charge because Si^{4+} can be partially replaced by Al^{3+} . However, the soil as a whole is electrically neutral, since this negative charge is balanced by the positive charge of various cations present in the soil (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , and H^+). The negative charge of anions of organic humic and fulvic acids present in the soil is also neutralized by such cations, in this case with a dependency on the degree of dissociation of the various acid functions, that is, increasing with pH. The capacity of the soil to bind cations is known as its CEC, often expressed in milliequivalents per 100 g (mEq/100 g) of soil. Strong sorption may be observed for cationic chemicals to the negatively charged clay minerals (Jarvis, 2016).

Green and Karickhoff (1990) suggested that the K_{oc} approach may no longer be appropriate when the ratio of clay to OC content exceeds 40%. In a study by von Oepen et al. (1991), in which the minimum OC content investigated was as high as 1.58%, it was concluded that “For more polar chemicals, e.g. acids (pH-dependent sorption) or amines, where sorption to clay minerals becomes important, it is impossible to obtain a soil-independent sorption coefficient, K_{oc} .” As well as the involvement of the mineral components of the soil, this variation may be due partly to the fact that soil organic matter does not have a single composition or structure and may be considered “a mixture of solid and semi-solid, bulk and thin film materials with a range of properties depending on the history and age of the sample” (Wauchope et al., 2002).

Low OC content

Aquifer soils (soils that hold groundwater) are prominent examples of low OC content media. Typical OC values of <0.1% are observed (Fox et al., 2017; Hartog et al., 2004; Lee & Park, 2013; Piwoni & Banerjee, 1989). This is much lower than that of typical European topsoils, which average between ~1.3 and ~4.5% OC in the upper 30 cm layer (Panagos et al., 2013). Jobbágy and Jackson (2000) noted that the OC content of a soil falls off sharply with increasing depth and that typical global OC values between 2- and 3-m depth are in the order of 0.05% to 0.4%, depending on the nature of the surface biome. Payne et al. (2008) also noted that “we have observed the use of default assumptions for OC fraction that exceed the values that we typically encounter by 10-fold, or more. This aquifer parameter is too critical to presume without sample collections, and the default assumption for aerobic aquifers should be very low, that is, 0.05%, or lower to be conservative.” Typical default values such as those used in the US EPA's Soil Screening User's Guide use a value of 0.2% when estimating migration

of chemicals to groundwater (US EPA, 1996), and the Brussels Region's Environmental Agency environmental risk assessment guidance (Bruxelles Environnement, 2019) specifies a default subsurface OC value of 0.1% for estimating the rate of lateral transport of groundwater pollutants within aquifers. Since laboratory K_{oc} determinations normally use topsoils (e.g., OECD 106 test guideline, OECD, 2000) at OC levels much higher than those found in aquifers, the difference in OC introduces uncertainties in the accuracy of the K_{oc} determination.

Nonlinear isotherms

Apart from noncompliance with the popular and convenient K_{oc} model, the sorption of organic chemicals to soils exhibits numerous deviations from the simple behavior embodied in the linear isotherm corresponding to the K_d metric. These complexities have been discussed in some detail by Wauchope et al. (2002) and others (Delle Site, 2001; Doucette, 2000) and are not reviewed here. However, it is clear that no simple metric (K_{oc} , K_d , Freundlich parameters) can fully capture the sorption behavior of a broad range of chemicals in a variety of soils. If a chemical follows Freundlich behavior, then its mobility at higher concentrations will be under-predicted by K_d or K_{oc} measurements made at lower concentrations and vice versa. Since environmentally relevant concentrations in subsurface soils and aquifers, due to degradation and dispersion/diffusion, are mostly below the concentrations used in adsorption studies, the environmentally relevant sorption is often underestimated by these indices.

Also, apparent K_d values are often lower when measured in sorption equilibration experiments than in ensuing desorption experiments in which the supernatant aqueous phase is replaced by a fresh aqueous phase. Consequently, the values of K_d lag behind the changes in the effect that is causing it, for example, slow diffusion or macromolecular interaction (Wauchope et al., 2002).

Slow kinetics and irreversible sorption

Sorption and desorption of chemicals do not reach equilibrium instantaneously but occur over time scales that reflect the kinetics of the complex series of steps involved (Beulke et al., 2004; Pignatello & Xing, 1996). Depending on the degree of mixing, rapid reversible diffusion of the sorbate and attachment to relatively accessible sites of the surface of soil constituents may occur in a matter of minutes. A slower, but fully reversible, second sorption phase requires between a few hours and 1–2 days. This has been attributed to slow diffusion within the pores and channels of the solid or limited molecular diffusion in the macromolecular organic matter. Depending upon the environmental matrix, the formation of irreversibly bound residues (also referred to as nonextractable residues [NER] and discussed below) may occur almost instantaneously. Finally, a very slow but reversible process, often referred to as “aged sorption,” occurs over a period of weeks to years. Since aged sorption is known to be a relevant and important

process restricting the leaching of pesticides through soils, guidance on how aged sorption studies should be conducted, evaluated and used in the regulatory leaching assessment was developed (EC, 2021b). Aged sorption studies can be performed using a range of approaches, including modified OECD 307 (OECD, 2002) and leaching in soil columns OECD 312 (OECD, 2004) and these have been described in an EC guidance document (EC, 2021b). This guidance includes advice on the risk assessment for plant protection products in groundwater. Aged sorption studies of this nature are relevant for plant protection products but are also applicable to chemical entities entering the terrestrial environment via sewage sludge applications to agricultural soils. The high OC content of sewage sludges (35% in primary sludge and 25% in digested sludge [Berthod et al., 2016]) can have a further significant influence on the adsorption-desorption characteristics of sludge-amended soils.

It should be emphasized that this level of experimental data is normally only available for plant protection products and some veterinary products. It is not normally available for other sectors including REACH-registered substances.

Nonextractable residues

Nonextractable residues, as the name implies, is defined as irreversibly adsorbed residues of a chemical entity that are not bioavailable in the dissolved phase on a timescale relevant for risk assessment (Schäffer et al., 2018). These residues cannot be extracted from an organic matrix (soil, sediment, sewage sludge, plant tissue) via the application of nondestructive, mild extraction approaches (ECETOC, 2013a). NER is operationally often defined as a material that is not extracted by different extraction methods (Davenport et al., 2022).

Formation of NER is a significant process, which limits the movement of chemicals through soils and sediments and the proportion of free chemicals in surface water. The intrinsic properties of a chemical influencing the level of NER formation have not been well captured to date (Ericson et al., 2014). Cao et al. (2020), and Loeffler et al. (2020) reported very high levels of NER formation for substances fulfilling the UBA proposed vM criteria like bisphenol S (45%), triclosan (28%–48%) and acetaminophen (80%–90%) after a few weeks of incubation in an oxic soil system. This highlights the importance to take NER formation as a relevant mitigating factor for mobility.

Nonextractable residues has been studied since the 1960s yet there is still no scientific consensus on how to characterize or address NER (Davenport et al., 2022; ECETOC, 2013b; Trapp et al., 2022). All NER extraction methods result in operationally determined NER fractions. Recent work has advocated a conceptual model and experimental extraction scheme to quantify and speciate various NER fractions, for example, biomass versus bound versus sequestered (Loeffler et al., 2020). However, it is widely acknowledged that the extraction methods have not been fully validated for regulatory purposes. Also, only a

limited number of chemical classes have been used in the experimental work. Kühne et al. (2016) have attempted to develop structural alerts for NER formation in soil. However, despite many approaches, they concluded that predicting NER formation was complex with many competing processes and a simple structure-based model was not feasible. They also concluded that there was insufficient data to develop more complex models.

Numerous studies have observed that NER formation is lower in abiotic control soil samples compared with microbially viable samples, which have received the same application rate and have been extracted using the same analytical procedures (e.g., Cao et al., 2020). This suggests involved role of microorganisms in NER formation (Barriuso et al., 2008; Cao et al., 2020). Incorporation via biogeochemical transformation on time scales exceeding a few days results in a chemical becoming the carbon source for resulting fractions such as humin, humic chemicals, humous, humic, and fulvic acids. Extreme changes in environmental conditions would be required to remobilize even the smallest quantities of residual chemicals associated with an aged soil (Horwath, 2007; Mordaunt et al., 2005).

The breadth and detail of the available work in this area remain limited and comparability between experiments is low, with studies having been performed over different time periods, on different chemistries with varying goals and conclusions (ECETOC, 2013a). Nonetheless, most of these studies have suggested that the remobilization of slowly desorbed or irreversibly bound residues is low and that the moiety released may be rapidly mineralized or degraded by microorganisms. This indicates that the environmental fraction attributed to NER within a soil profile will not undergo leaching across different soil horizons. Thus, chemicals that form high amounts of NERs in sediment and soil experiments are considered P under REACH, even if their mobile and bioavailable fraction degrades rapidly. As shown with the few examples above, this can happen to chemicals that fulfill the K_{oc} -based criteria for M/vM. Also, chemical residues that are strongly adsorbed to sediment or soil material should be considered a low priority for the protection of sources of drinking water.

Competitive sorption

Numerous cases of competition for sorption sites have been reported. Examples include xenobiotic organic cations being displaced by the inorganic cations of salts present in pore water (Doucette, 2000); glyphosate herbicide being displaced by phosphate used as a fertilizer (Munira et al., 2018); and the short-chain perfluoroalkyl carboxylic acid anion $C_3F_7COO^-$ being displaced by longer-chain (more hydrophobic) perfluoroalkyl carboxylates and sulfonates (Gellrich et al., 2012). The current lack of knowledge of the details of these processes makes them hard to predict and they are currently only studied in detail on a case-by-case basis.

In this section, it has been highlighted that using the K_{oc} model for assessing soil sorption is an over-simplified model

and should be treated with caution. This paper indicates some of the complexities involved in understanding the mobility of chemicals in soils and proposes a scientific-based tiered approach to refine the screening of chemicals for the potential to leach. Similar complexities also arise in sediments too but have generally not been studied so extensively.

ALTERNATIVE APPROACHES FOR IDENTIFYING M and vM CHEMICALS

The use of K_{oc} (or D_{ow} or K_{ow}) is insufficient to characterize mobility in the environment, as fate and partitioning processes differ depending on the environmental compartment. Clearly, a substance with a short degradation half-life in soil is less likely to leach from soil to groundwater irrespective of its mobility, compared to one that has a slower degradation half-life in soil and of equal mobility (Kalberlah et al., 2014).

The UBA proposed M/vM cut-off criteria of Log K_{oc} 4 and 3, respectively, may not permit sufficient discrimination to allow an efficient prioritization of chemicals with potential mobility concerns. Based on a simple qualitative comparison of the UBA M/vM classifications with the classifications of McCall and FAO (Supporting Information: Tables S1–S3), one can see that the UBA cut-off for vM combines (approximately) the top 3 mobility classes of McCall and FAO, thus reducing discrimination. Similarly, there is a lack of discrimination for immobile classifications. Consequently, the proposed scheme may lead to an over-identification of candidates of suspected mobility, resulting in burdensome follow-up requirements for both regulators and submitters alike. Furthermore, whilst the proposed classification uses a combination of “P,” “M,” and “T,” the potential for refinement of “P” and “T” is often limited in practice, thereby potentially placing high emphasis on the ability to refine “M” in the PMT assessment. This again highlights the need to carefully consider the appropriateness of simple adsorption models, and to be able to employ higher tier assessment methods when appropriate, based on the weight of evidence available.

As an alternative, ECETOC (2021) has proposed a tiered approach to characterizing potential human exposure to contaminants in sources of drinking water. The tiered approach takes into consideration the chemical's use patterns, compartments of environmental release, release rates, as well as the chemical's fate and partitioning properties.

A screening level exposure assessment could use tools such as the GUS index (Groundwater Ubiquity Score index, Gustafson, 1989), the prioritization approaches for the Groundwater Watch List (GWWL) (CIS WG GW, 2018) and the SCI-GROW model (Screening Concentration In GROund Water, US EPA, 2003), elements of which could be further developed to consider the interaction of degradation, mobility and emissions. The alternative approaches are examined below.

Leaching indices

The need for a simultaneous or joint assessment of the competition between migration and degradation during

transport through the soil profile was proposed for nonpolar pesticides by Gustafson (1989). This approach enables leachability (a property combining both degradation and migration rates) to be ranked in terms of the GUS Index:

$$GUS = \log(t_{1/2, \text{soil}}) \times (4 - \log K_{oc}),$$

where $t_{1/2, \text{soil}}$ is the degradation half-life of the chemical in soil, expressed in days.

This approach potentially provides greater flexibility than the use of separate criteria for P/vP and M/vM, since data from leachability studies could be used directly (i.e., without requiring separate experiments to determine “M” and “P”). Gustafson considered that “potential leachers” are those for which $GUS > 2.8$, while “nonleachers” would have $GUS < 1.8$ leaving a transition zone of moderate leachability between these two cut-off values (Gustafson, 1989). The GUS index is discussed in the UBA report (Neumann & Schliebner, 2019) where it is shown that P/vP and M/vM criteria theoretically give similar GUS indices, but no consideration is given to the possibility of using the GUS index-based data from leachability studies. Possibilities to develop this concept further, for example to consider the relevance or otherwise of K_{oc} , are discussed in the following sections of this paper.

While the GUS index has been one of the most commonly used chemical transport metrics in assessing nonpolar pesticide leachability, many other indices have been proposed. A total of 15 such indices for assessing pesticide leaching potentials have been reviewed by Akay Demir et al. (2019). Most of these indices are based on similar principles to the GUS index, requiring parameters for sorption strength (generally expressed by K_{oc}) and half-life in soil and ignoring aquatic degradation or partitioning of ionizable chemicals.

Where there is sufficient data, a detailed modeling approach for defining the relative and absolute leachability of chemicals is recommended by ECETOC (2021). However, many chemicals lack sufficient data and therefore leachability indices may be useful for preliminary screening and prioritization purposes. A further limitation of this approach is the lack of an exposure assessment. This has also been recognized by the GWWL approach (CIS WG GW, 2018), but a suitable methodology has not yet been fully developed and relies on a case-by-case justification of the environmental (groundwater) exposure.

Common Implementation Strategy Working Group Groundwater watch list approach

The European Commission's Common Implementation Strategy Working Group Groundwater (CIS WG GW) has developed a methodology to prioritize substances for inclusion on a Groundwater Watch List (GWWL) of existing chemicals to be monitored voluntarily in groundwater by Member States (CIS WG GW, 2018; Lapworth et al., 2019). The prioritization process contains both prospective and retrospective elements; the prospective elements utilize predictive models to identify substances of potential concern, whilst the retrospective elements utilize monitoring

data. Like other approaches discussed above, the prospective element is simplistic in terms of leaching indices as it is based on the K_{oc} or K_{ow} , therefore the same opportunities exist for potential refinement for ionizable compounds as discussed above. The retrospective element is only useful if monitoring data are available, which for the purpose of identifying “M” and “vM” substances will not be directly applicable for most compounds. However, where monitoring data exist, these can be highly useful to “ground-truth” the more predictive elements of the prioritization process, for example, if substances prioritized based on predictive models are not detected at the concentrations expected in the environment, then this may lead to follow-up studies so that the models can be improved.

Modeling approaches

Human exposure to chemicals via drinking water is included in predictive risk assessment approaches from the WHO (World Health Organization), US-EPA and European regulations and these have recently been reviewed by ECETOC (2021). Approaches and the related quantitative models differ as the regulatory focus is different. Models for industrial chemicals take into account the life-cycle of the chemical by integration of information on use patterns and potential environmental releases, while approaches for pesticides typically focus on the routes of exposures associated with the application to crops.

A targeted evaluation of the potential for transport to groundwater requires information on the compartment of release to the environment, the level of emissions, and the fate and partitioning characteristics of the chemical under realistic environmental scenarios. For example, for chemicals reaching groundwater from the application of sewage sludge to land, a prerequisite for potential exposure in groundwater is the adsorption of the chemical to sewage sludge and the use of sludge as a fertilizer to land. In these cases, the subsequent desorption from the sludge and further sorption/desorption in the soil layers should be considered. For soil-applied chemicals, a mobility cut-off criterion based on soil adsorption (K_{oc}) alone should be considered at an initial screening level only, whereas the potential for transport to drinking water can be assessed by the use of tiered risk assessment models. As the K_{oc} is a classical metric to inform environmental partitioning, model parametrization should be reviewed in light of the relevance of this parameter for the assessed substance. Iteration in model parametrization (Figure 3), including refinements on environmental release, partitioning, and distribution, enables refined prediction of the potential for exposure in drinking water.

In the exposure evaluation of pesticides, a variety of models have been used to assess concentrations in surface and groundwater, from screening level to higher tier models. For groundwater, an initial assessment using the SCI-GROW model (US EPA, 2003) was widely used in the USA. The SCI-GROW estimate is based on simple environmental fate properties of the pesticide (aerobic soil

degradation half-life and linear adsorption coefficient normalized for soil OC content, K_{oc}) and the application rate. SCI-GROW provides conservative estimates of pesticides in groundwater, but it does not have the capability to consider variability in the leaching potential of different soils, weather, cumulative yearly applications or depth to aquifers. The model is helpful as an early screening tool, particularly where limited data are available. Also, it should be noted that the SCI-GROW model was only validated with K_{oc} values in the range of 32 to 180 L/kg (log K_{oc} = 1.5 to 2.3) and has an upper K_{oc} input limit of 9995 L/kg (log K_{oc} = 4). SCI-GROW has not been implemented within the European plant protection product regulatory framework, where more complex FOCUS (FORum for Co-ordination of pesticide fate models and their USE) models have been deployed.

Significant work has been performed by the FOCUS model initiative for modeling plant protection product movement to groundwater (EC, 2014). Four FOCUS models (PELMO [PEsticide Leaching Model], PRZM [Pesticide Root Zone Model], PEARL [Pesticide Emission Assessment at Regional and Local scales], and MACRO [MACROpore flow model]) are used in Europe for the first-tier assessment of the leaching potential of pesticides to groundwater. The modeling endpoint is the average annual leachate concentration at a depth of 1 m representing a conservative approach for shallow groundwater close to the soil surface. The scenarios are generic and do not mimic specific fields but are designed to represent realistic worst-case scenarios that describe an overall vulnerability approximating the 90th percentile of possible situations that would enable the leaching of a chemical from different soil types, that is, high rainfall and low OC soils.

These groundwater model scenarios are based on Europe as it existed between 1997 and 2000 when they were developed. The EU has since grown and changed, but the existing scenarios were found to be fit for purpose and provide regulators with a conservative estimate for the leaching potential of pesticides to groundwater for the whole EU (EC, 2014).

The transport of a chemical to drinking water is an integral part of the exposure assessment framework used in European regulations for the registration and management of industrial chemicals (EC, 2006). The main environmental risk assessment tool is the EUSES (European Union System for the Evaluation of Substances) model, which has recently been coded into several newer applications in support of REACH registrations (e.g., ECHA's CHEMical Safety Assessment and Reporting tool [CHESAR], ECHA, 2021 and ECETOC's Targeted Risk Assessment [TRA] tool, ECETOC, 2014).

The EUSES model includes indirect exposure of humans via drinking water. EUSES assumes drinking water is sourced either from groundwater or surface water; both are assessed in the model and the source that results in the highest exposure is used in the assessment. For the groundwater scenario, exposure via sewage sludge

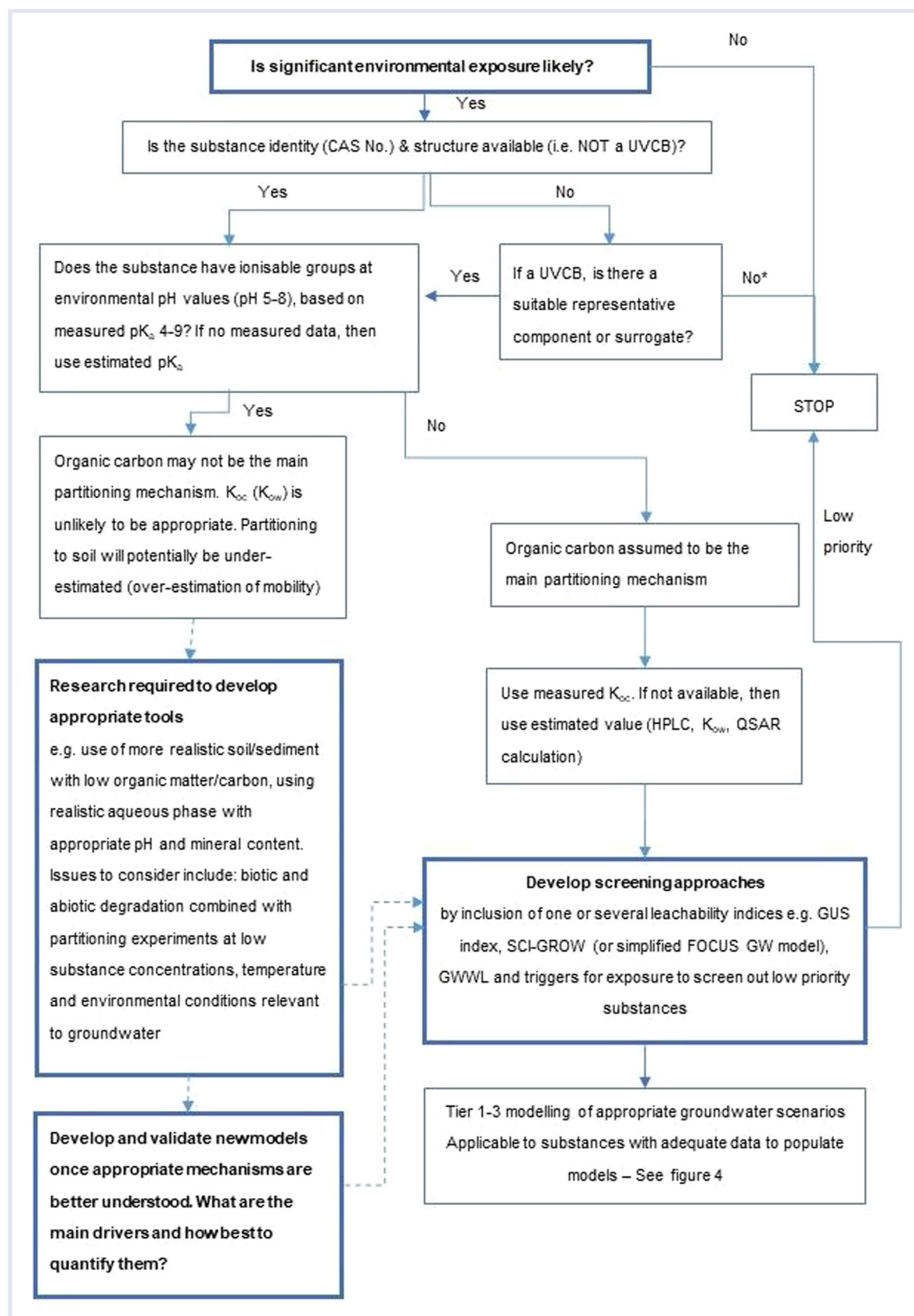


FIGURE 3 ECETOC tiered approach for the assessment of drinking water safety: Tier 0 screening for mobility in groundwater. Boxes in bold point to science gaps, for which additional research is required. Reproduced with permission from ECETOC (2021). The asterisk indicates where further information related to the identification of representative components or surrogates may be required

application to land is considered the dominant route of exposure, with groundwater concentrations assumed to be equivalent to pore-water concentrations in topsoil after 10 years of sludge application, and therefore provides a worst-case estimation of exposure in groundwater. For the surface water scenario, the model assumes storage of surface water in open reservoirs and via dune treatment with consideration of water purification. However, screening level risk assessment would, in the absence of fate simulation studies in surface water, exclude consideration of purification, thus defaulting back to surface water concentration as a relevant input to inform the concentration in drinking water.

Other potential sources of drinking water exposure include the use of surface water for irrigation and the extraction of raw drinking water via riverbank filtration, which are not specifically considered in EUSES. In particular, the EUSES model does not include a compartment for raw water sourced from surface water (similar to groundwater), thus excluding specific considerations of hydraulic flows and fate processes in river banks. Whether these omissions are important or not is a question that requires further research, particularly with regard to bank filtration, which is currently only included in the surface water component of the drinking water module in EUSES.

Higher tier assessments for groundwater can be performed if sufficient data are available. For REACH chemicals, these data are not generally available, so estimates or default values (as used in FOCUS for subsoil degradation) or additional experimental data would be required before results from such models could be considered. Furthermore, the models used should ideally always match the complexity of the data available, that is, if higher tier data exist then higher tier models should be used.

Another consideration is the level of drinking water treatment that should be taken into account in models. On the one hand, current best practices in drinking water treatment are well established and are increasingly being used (e.g., the WHO have published guidelines for drinking-water quality, which detail current treatment processes for the removal of chemical contaminants [WHO, 2017]). On the other hand, the EU drinking water directive (EU, 2020) states that risk assessment and risk management of the catchment areas for abstraction points should take a holistic approach and be geared toward reducing the level of treatment required for the production of water intended for human consumption. In practice, a balanced approach considering improvement trends in drinking water treatment seems sensible, so that “worst-case” assumptions can be checked and refined accordingly.

THE ECETOC TIERED APPROACH

In order to address the potential for human exposure to contaminants in drinking water, ECETOC (2021) has proposed a tiered assessment approach, based on scientific principles, to utilize screening levels or more advanced models, depending on the nature of the data available.

At a screening level, the ECETOC approach proposes exposure assessment tools such as the previously mentioned GUS index, GWWL, and SCI-GROW. The approach considers the interaction of degradation, mobility and emissions, resulting either in an exposure index or an expected worst-case concentration (if the emission is considered significant). If necessary, modeling approaches can be deployed to aid the identification of those chemicals with potential concern for indirect exposure of humans via drinking water. Those chemicals requiring further iterations in the risk assessment procedure would be examined in more detail using higher tier assessments, for example, refined emission rate predictions, increased environmental fate understanding or the use of higher tier models. ECETOC recognized that for many chemicals, for example, ionizable chemicals, the use of K_{oc} , D_{ow} , or K_{ow} to describe mobility is not appropriate. Currently, suitable tools are not available to address these shortcomings, and this should be a priority for future research.

ECETOC proposed a tiered approach for the assessment of drinking water safety, including an exposure assessment focused on sources of drinking water (Figures 3 and 4). After the initial screening (Tier 0; Figure 3), those chemicals with significant potential to migrate to drinking water sources move to Tier 1 modeling (Figure 4), which focuses on the routes of exposure for drinking water including from ground and surface water via bank filtration. Bank filtration systems are common in the Netherlands, where river banks or dunes are essentially used as natural filters. Extraction is typically from a well close to a source of surface water, which provides “recharge” as the well water is abstracted. In EUSES, the bank filtration system is addressed by using a simple “purification” factor, which is intended to represent a reasonable worst case (i.e., minimal removal) for this exposure scenario. However, it is not addressed at all in most higher tier models. This has been recognized as a gap by the European chemical industry council (Cefic) Long-range Research Initiative (LRI), which has initiated research to address this (Cefic, 2021). The Cefic LRI project (ECO 54) aims to develop lower- and higher-tier models, including consideration of bank filtration, for human exposure to chemical substances through drinking water sources. The ECETOC Tier 1 assessment can also guide the relevant route of exposure to be considered in higher tier assessments. If required, the Tier 2 models (Figure 4) aim to increase the realism in the exposure assessment to estimate the transport from soil to groundwater where sufficient data exists. Iterations in the exposure assessment in groundwater at Tier 3 (Figure 4) may include the use of refined information at the level of emissions to soil, the fate and partitioning information from measured data and/or the characteristics of the soil compartment. For nonpesticide chemicals, a lack of experimental and field data generally makes using these higher tier approaches a challenge, which underlines the importance of developing a robust screening tier (Tier 0).

The ECETOC Tier 0 (Figure 3) builds on the UBA proposal, but it first examines the suitability of the chemical for

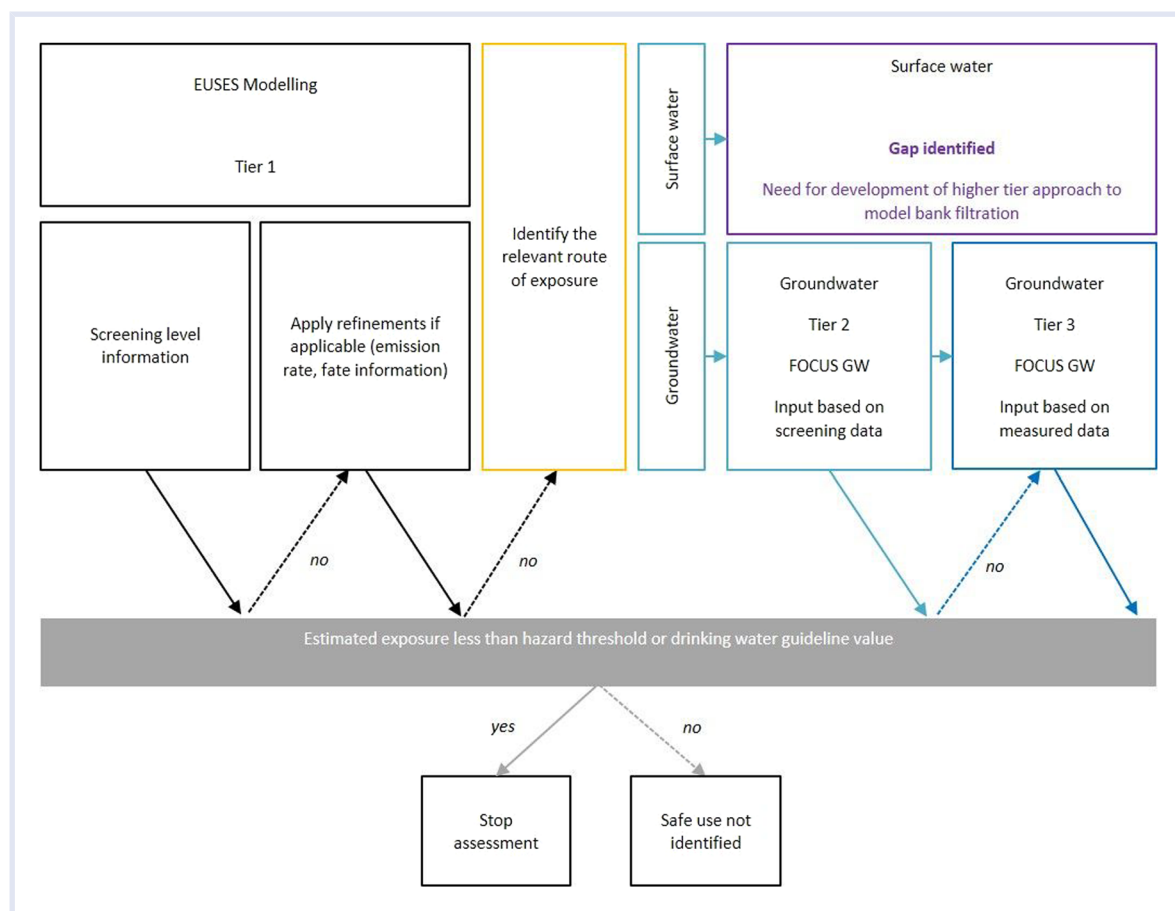


FIGURE 4 ECETOC tiered approach for the assessment of drinking water safety: Tier 1, 2 and 3 exposure modeling. Reproduced with permission from ECETOC (2021)

consideration as a potential surface or groundwater contaminant. Exposure to drinking water sources may occur if significant releases to the environment occur. The potential for significant exposure might be excluded based on used information, for example, intermediates or closed systems. The exposure assessment of industrial chemicals accounts for scenarios from multiple uses and estimates of exposure are derived on the basis of generic exposure scenarios for all registered uses. Release pathways and worst-case conservative values of amounts of release are characterized for a wide variety of applications, as reported in SpERC (Specific Environmental Release Category) scenarios (Cefic, 2012). During the screening assessment, it would be beneficial to have an exposure scoring system. The Cefic LRI project ECO 54 (Cefic, 2021) aims to develop a scoring system that integrates chemical tonnage, use patterns and substance properties.

The second step in Tier 0 is to identify the chemical and examine its structure and existing measured physico-chemical data. If the chemical cannot be characterized, for example, it is classified as a UVCB (Unknown or Variable composition, Complex reaction products, or of Biological materials), then it cannot be assessed as a whole for potential to migrate to drinking water and will not be identified

in any standard analytical monitoring program. In such cases, the assessment needs to focus on constituents of concern. If the UVCB contains a suitable representative component or surrogate, then this can be considered in the scheme.

In the next step of Tier 0, the chemical is assessed to see if K_{oc} is likely to be a suitable preliminary screening parameter for mobility in soil/sediment/sewage sludge. As previously discussed, if the chemical has ionizable groups at environmental pH values (typically pH 5–8), K_{oc} may be a poor descriptor of its mobility. Typically, pH values 2 log units on either side of the pK_a indicate that the ionizable group will be almost completely ionized or nonionized (depending upon the moiety of the molecule, e.g., acid or base). However, pH values 1 log unit on either side of the pK_a indicate approximately 10% ionization, so for chemicals with one or more pK_a values in the range of pH 4–9 (i.e., acids with $pK_a > 4$ or bases with $pK_a < 9$), the relevance of K_{oc} is likely to be particularly uncertain and not suitable for classification. This is a relatively conservative pK_a range and other researchers, for example, Franco et al. (2010), have suggested that ionizable chemicals should be defined as acids with $pK_a > 2$ or bases with $pK_a < 12$, based on more extreme environmental pH values.

The partitioning of ionizable chemicals is very complex, and a range of soil/sediment properties may influence the sorption behavior, such as CEC, soil pH, clay content, and so forth. The use of a more realistic subsurface soil/sediment with low OC using realistic aqueous phase concentrations with appropriate pH and mineral content may yield more helpful normalization methods to describe the mobility of such chemicals.

Other issues relevant to subsurface soils include questions such as, can biotic and abiotic degradation rates be combined with partitioning at low chemical concentrations and what effects do temperature and environmental conditions relevant to groundwater have on the processes? These areas require further research to develop and validate new models based on a better mechanistic understanding.

In the meantime, it is not scientifically valid to assume that all chemicals fit the K_{oc} model sufficiently to be recommended for determining a chemical's mobility in the environment, in particular in an “in or out” classification scheme where chemicals that fall in will get banned from the market.

Mobility and soil degradation half-life are considered in combination at Tier 0 of the ECETOC proposal. Those chemicals with a low potential for reaching groundwater, for example, “nonleachers” with GUS < 1.8, are no longer considered a risk for groundwater. For chemicals already in commercial use, if monitoring data suggests a significant exposure, then a more detailed investigation would be warranted, including efforts to understand how, why and where these chemicals have been detected.

Both UBA's and ECETOC's proposals have limitations and this highlights some important scientific gaps that require substantial research before the adequate prediction of a chemical's transport to drinking water sources can be made with sufficient reliability for regulatory purposes. These research needs are summarized in the next section.

In order to comply with the EU commission's proposal for the introduction of new hazard classes for PMT and vPvM substances, it is acknowledged that an exposure-based approach would not be considered as being applicable for a purely property-based identification of substances of concern. Whether a substance is capable of reaching drinking water resources derived from either groundwater or river-bank filtration, the derivation of a leachability index could be considered an important element of the weight of evidence needed to assess M/vM properties of substances for which K_{oc} is an arguable determinant. This leachability index could be derived either experimentally through a soil column leachability study (OECD 312) or by the use of an in silico tool.

RESEARCH NEEDS TO UNDERSTAND THE KEY MECHANISMS DICTATING THE MOBILITY OF CHEMICALS IN SURFACE AND GROUNDWATER

Some knowledge gaps have been identified in this paper, which makes the prediction of chemical mobility potentially unreliable. To better understand mobility, the following research targets have been identified:

- Developing more appropriate screening metrics for assessing mobility, especially for ionizable chemicals.
- Understanding the effects of low OC in subsurface soil and sediment on the measurement of mobility. The influence of matrix properties such as mineral content on chemical mobility should also be considered.
- The use of improved aged sorption studies and realistic application and exposure scenarios for chemicals entering soils via indirect application should be encouraged based on the principles outlined in the testing proposal SANTE/12586/2020—REV 0 26 January 2021, entitled “Guidance on how aged sorption studies for pesticides should be conducted, analyzed and used in regulatory assessments” (https://ec.europa.eu/food/system/files/2021-01/pesticides_ppp_app-proc_guide_fate_aged-sorption.pdf), and, any subsequent updates thereof.
- Develop new tools to concentrate, separate and detect low concentrations of chemicals in surface and groundwater, especially for ionizable and hydrophilic chemicals, which can present significant technical challenges. This is also particularly relevant to the consideration of metabolites, which are normally relatively hydrophilic chemicals.
- Use this improved understanding to develop modeling techniques to determine mobility characteristics of chemicals, especially ionizable chemicals. The improved knowledge of the processes involved in bank filtration should also be incorporated into environmental distribution models.
- Additional research is needed with respect to mobility in terms of the evaluation of both UVCBs and polymers, as available standardized test methods and available exposure estimation models are currently not applicable to these kinds of substances.

Using the research findings highlighted above will also aid the interpretation of robust groundwater monitoring data with the aim of identifying the main influencing factors and mechanisms leading to detection under environmentally realistic conditions.

CONCLUSIONS

Several EU water policies (Water Framework Directive, Ground Water Directive, and Drinking Water Directive) aim for the protection of the surface, ground, bathing, and drinking water. Furthermore, EU chemical regulations for plant protection products, biocides, medicinal products (covering human and veterinary pharmaceuticals), and industrial chemicals (i.e., those registered under REACH) already cover, to a certain extent, groundwater exposure and/or risks to humans via consumption of drinking water, as part of the required risk assessment. The PMT/vPvM concept developed by UBA relies on chemical property-based criteria for the identification of potential drinking water contaminants. Evaluation of the proposed P/vP and M/vM criteria by ECETOC against available monitoring data did not reveal any relationship between P and

log K_{oc} and the detection of chemicals in surface and groundwater.

The simple mobility criterion of a threshold $K_{oc}/D_{ow}/K_{ow}$ value in the UBA concept is thus too simplistic to be used as a standalone in a hazard-based regulation like CLP where chemicals are either “in or out.” It does not consider use patterns and associated environmental emissions, the complex behavior chemicals can undergo in soils and sediments or the likely influence of the environmental concentration of the chemical. Alternative approaches such as utilizing leaching indices, additional exposure criteria, and more sophisticated process-oriented leaching or groundwater models offer potential refinements, depending on the type of data available; however, most of these approaches also predict mobility based on K_{oc} , D_{ow} , or K_{ow} . Leachability data obtained experimentally, for example, based on OECD 312 (OECD, 2004) or based on aged sorption studies for pesticides (EC, 2021b), may give a better indication of the mobility of a chemical under simulated environmental conditions, but these also have limitations; for example, the standard tests focus on surface soil layers and do not address conditions found in subsurface soil layers or in sediments. Ultimately, the widespread use of K_{oc} , D_{ow} , and K_{ow} , together with the high uncertainty in using them to predict mobility, highlights the need for the development of more reliable approaches, particularly for ionizable compounds, and a number of research needs have been identified in this paper to facilitate this.

A tiered approach has been proposed by ECETOC, where an initial Tier 0 screening level risk assessment, using tools such as the GUS index, GWWL, and SCI-GROW, develops the UBA proposal further to include combined degradation and mobility along with an exposure element. Where appropriate mobility metrics still need to be developed, particularly for ionizable compounds, as these become available they may be incorporated into higher tier models (Tiers 1–3 in the ECETOC approach).

The impact of NER formation on the PMT/vPvM concept is complex and not fully understood. It may depend on the functional groups in the parent/metabolite and the composition of the environmental matrix. Its impact on mobility is, nevertheless, radical, resulting in almost total immobilization of chemical moieties over a prolonged timeframe.

The ECETOC work group recognizes the use of simplified indicators of adsorption, such as K_{oc} , D_{ow} , and K_{ow} as the initial, Tier 0, screening step in a leachability assessment procedure, and, herein, describes the application of three further Tiers of assessment. Tier 1 introduces routes of exposure and Tier 2 and Tier 3 incorporate more scientifically relevant derived parameters permitting a more realistic evaluation while remaining conservative yet with an acceptable discriminatory screening capacity. This includes the proposal to use a leachability index approach in order to comply with the EU commission's proposal for the introduction of new hazard classes for PMT and vPvM substances.

ACKNOWLEDGMENT

The authors would like to thank the ECETOC Scientific Committee for their valuable comments during the preparation of this manuscript. This work was conducted as part of the European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) Task Force “Persistent Chemicals and Water Resources Protection” (2020–2022). The authors' time to contribute to this review was supported by their organizations. There are no funders to report for this submission.

DISCLAIMER

Not applicable.

AUTHOR CONTRIBUTIONS

Sascha Pawlowski: Conceptualization (equal); methodology (equal); writing—original draft preparation (equal); writing—review and editing (equal). **Lothar Aicher:** Conceptualization (equal); methodology (equal); writing—original draft preparation (equal); writing—review and editing (equal). **Albert Berends:** Conceptualization (equal); methodology (equal); writing—original draft preparation (equal); writing—review and editing (equal). **Pippa Curtis-Jackson:** Conceptualization (equal); methodology (equal); writing—original draft preparation (equal); writing—review and editing (equal). **Andreas Häner:** Conceptualization (equal); methodology (equal); writing—original draft preparation (equal); writing—review and editing (equal). **Juliane Hollender:** Conceptualization (equal); methodology (equal); writing—original draft preparation (equal); writing—review and editing (equal). **Bernhard Jene:** Conceptualization (equal); methodology (equal); writing—original draft preparation (equal); writing—review and editing (equal). **Karen Jenner:** Conceptualization (equal); methodology (equal); writing—original draft preparation (equal); writing—review and editing (equal). **Aaron Redman:** Conceptualization (equal); methodology (equal); writing—original draft preparation (equal); writing—review and editing (equal). **Gordon Sanders:** Conceptualization (equal); methodology (equal); writing—original draft preparation (equal); writing—review and editing (equal). **Nathalie Vallotton:** Conceptualization (equal); methodology (equal); writing—original draft preparation (equal); writing—review and editing (equal). **Neil Wang:** Conceptualization (equal); methodology (equal); writing—original draft preparation (equal); writing—review and editing (equal). **James R. Wheeler:** Conceptualization (equal); methodology (equal); writing—original draft preparation (equal); writing—review and editing (equal).

CONFLICT OF INTEREST

The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

All data used are either publicly available through the published articles cited, the ECETOC Technical Report No. 139 (<https://www.ecetoc.org/wp-content/uploads/2021/10/ECETOC-TR-139-Persistent-chemicals-and-water-resources-protection-2.pdf>) or via the ECHA webpage (<https://chesar>).


echa.europa.eu/home; https://echa.europa.eu/documents/10162/17224/information_requirements_r11_en.pdf/a8cce23f-a65a-46d2-ac68-92fee1f9e54f?t=1498475968629; https://echa.europa.eu/documents/10162/17224/information_requirements_r16_en.pdf/b9f0f406-ff5f-4315-908e-e5f83115d6af?t=145553705739.


SUPPORTING INFORMATION

Tables S1–S3. Overview of various log K_{oc} thresholds and associated mobility classes.

ORCID

Andreas Häner  <http://orcid.org/0000-0003-0815-5579>

Juliane Hollender  <http://orcid.org/0000-0002-4660-274X>

Aaron Redman  <http://orcid.org/0000-0002-5933-7906>

James R. Wheeler  <http://orcid.org/0000-0002-9162-5035>

REFERENCES

- Akay Demir, A. E., Dilek, F. B., & Yetis, U. (2019). A new screening index for pesticides leachability to groundwater. *Journal of Environmental Management*, 231, 1193–1202.
- Arp, H. P., & Hale, S. E. (2019). *REACH improvement of guidance and methods for the identification and assessment of PMT/vPvM substances*. vol Texte 126/2019. Umweltbundesamt.
- Barriuso, E., Benoit, P., & Dubus, I. G. (2008). Formation of pesticide non-extractable (bound) residues in soil: Magnitude, controlling factors and reversibility. *Environmental Science & Technology*, 42(6), 1845–1854.
- Beltman, W. H. J., Boesten, J. J. T. I., & van der Zee, S. E. A. T. M. (2008). Spatial moment analysis of transport of nonlinearly adsorbing pesticides using analytical approximations. *Water Resources Research*, 44(5), 1–12.
- Berthod, L., Roberts, G., Sharpe, A., Whitley, D. C., Greenwood, R., & Mills, G. A. (2016). Effect of sewage sludge type on the partitioning behaviour of pharmaceuticals: A meta-analysis. *Environmental Science: Water Research and Technology*, 2(1), 154–163.
- Beulke, S., Brown, C. D., Fryer, C. J., & van Beinum, W. (2004). Influence of kinetic sorption and diffusion on pesticide movement through aggregated soils. *Chemosphere*, 57(6), 481–90. <https://doi.org/10.1016/j.chemosphere.2004.06.026>
- Bruxelles Environnement. (2019). *Sous division Sols—Code de bonnes pratiques pour l'étude de risque*. Version 31.05.2019. https://environnement.brussels/sites/default/files/cbp_etude_de_risque_fr.pdf
- Cao, S., Wang, S., Zhao, Y., Wang, L., Ma, Y., Schäffer, A., & Ji, R. (2020). Fate of bisphenol S (BPS) and characterization of non-extractable residues in soil: Insights into persistence of BPS. *Environment International*, 143, 105908.
- Carvalho, R. N., Marinov, D., Loos, R., Napierska, D., Chirico, N., & Lettieri, T. (2016). *Monitoring-based exercise: Second review of the priority substance list under the water framework directive (final draft version)*. European Commission, DG Joint Research Centre Institute for Environment and Sustainability. https://circabc.europa.eu/sd/a/7fe29322-946a-4ead-b3b9-e3b156d0c318/Monitoring-based%20Exercise%20Report_FINAL%20DRAFT_25nov2016.pdf
- Cefic. (2012). *Cefic Guidance Specific Environmental Release Categories (SPERCs). Chemical Safety Assessments, Supply Chain Communication and Downstream User Compliance*. October 2012. Revision: 2. Prepared by the Cefic SPERC Core Team. <https://cefic.org/app/uploads/2019/01/SPERCs-Specific-Environmental-Release-Classes-REACHImpl-ES-CSA-CSR.pdf>
- Cefic. (2021). *LRI ECO 54: Developing a tiered modelling framework in support of risk assessment of chemical chemicals associated with mobility concerns*. <https://cefic-lri.org/projects/eco-54-developing-a-tiered-modeling-framework-in-support-of-risk-assessment-of-chemical-substances-associated-with-mobility-concerns/>
- CIS WG GW. (2018). *Voluntary Groundwater Watch List Concept & Methodology, Technical Report based on final draft 12.3, endorsed by CIS Working Group Groundwater (WG GW)*. <https://circabc.europa.eu/ui/group/9ab5926d-bed4-4322-9aa7-9964bbe8312d/library/d3fa0178-0134-4316-a11c-dcfd71efca69/details/1.0>
- Davenport, R., Curtis-Jackson, P., Dalkmann, P., Davies, J., Fenner, K., Hand, L., McDonough, K., Ott, A., Ortega-Calvo, J. J., Parsons, J., Schäffer, A., Sweetlove, C., Trapp, S., Wang, N., & Redman, A. (2022). Scientific concepts and methods for moving persistence assessments into the 21st Century. *Integrated Environmental Assessment and Management*, 18(6), 1454–1487. <https://doi.org/10.1002/ieam.4575>
- Delle Site, A. (2001). Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. A review. *Journal of Physical and Chemical Reference Data*, 30(1), 187–439.
- Doucette, W. J. (2000). Soil and sediment sorption coefficients. In R. S. Boethling & D. Mackay (Eds.), *Handbook of property estimation methods for chemicals* (1st ed., pp. 141–188). Lewis Publishers, CRC Press.
- Environment Agency (EA). (2019). *Monitoring database maintained by the Environment Agency held in the WHIMS database*. Accessed June 7, 2019.
- EC. (2006). Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC. *Official Journal of the European Union*.
- EC. (2008). Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006. (OJ L 353, 31.12.2008. p.1).
- EC. (2009). Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC. *Official Journal of the European Union*.
- EC. (2014). *Assessing Potential for Movement of Active Substances and their Metabolites to Ground Water in the EU*. Report of the FOCUS Ground Water Work Group, EC Document Reference Sanco/13144/2010 version 3, 613p.
- EC. (2020a). EUROSTAT DataBase. European Commission. <https://ec.europa.eu/eurostat/data/database>
- EC. (2020b). Communication from the Commission to the European Parliament, The Council, The European Economic And Social Committee and the Committee of the Regions. Chemicals Strategy for Sustainability. Towards a Toxic-Free Environment. COM/2020/667 final.
- European Commission (EC). (2021a). Note for the attention of Mr Bjorn Hansen, Executive Director, ECHA. Request for support to the impact assessment on the planned revision of the REACH Regulation. Ref. Ares (2021) 2470219—12/04.2021.
- EC. (2021b). Guidance on how aged sorption studies for pesticides should be conducted, analysed and used in regulatory assessments, EC Document Reference SANTE/12586/2020—REV 0, 26 January 2021, 82.
- ECETOC. (2013a May). *Understanding the relationship between extraction technique and bioavailability*. Technical Report No. 117. <https://www.ecetoc.org/wp-content/uploads/2014/08/ECETOC-TR-117-Understanding-the-relationship-between-extraction-technique-and-bioavailability.pdf>
- ECETOC. (2013b, May). *Development of interim guidance for the inclusion of non-extractable residues (NER) in the risk assessment of chemicals*. Technical Report No. 118. <https://www.ecetoc.org/wp-content/uploads/2014/08/ECETOC-TR-118-Development-of-interim-guidance-for-the-inclusion-of-non-extractable-residues-NER-in-the-risk-assessment-of-chemicals.pdf>
- ECETOC. (2014). *Targeted Risk Assessment (TRA) tool*. <https://www.ecetoc.org/targeted-risk-assessment-tra/>
- ECETOC. (2021, May). *Persistent chemicals and water resources protection*. Technical Report No. 139. <https://www.ecetoc.org/wp-content/uploads/2021/10/ECETOC-TR-139-Persistent-chemicals-and-water-resources-protection-2.pdf>

- Ericson, J. F., Murray-Smith, R., Roberts, G., Hannah, B., Hoeger, B., & Ryan, J. (2014). Experiences with the OECD 308 transformation test: A human pharmaceutical perspective. *Integrated Environmental Assessment and Management*, 10(1), 114–124.
- European Chemical Agency (ECHA). (2016). Chapter R.16: Environmental exposure assessment. In *Guidance on information requirements and Chemical Safety Assessment, Version 3.0* (pp. 1–178). ECHA.
- European Chemical Agency (ECHA). (2017). Chapter R.11: PBT/vPvB assessment. In *Guidance on information requirements and Chemical Safety Assessment, Version 3.0* (pp.1–158). ECHA.
- European Chemical Agency (ECHA). (2021). *CHEMical Safety Assessment and Reporting tool (CHESAR)*. <https://chesar.echa.europa.eu/home>
- European Medicines Agency (EMA). (2006). *Guideline on the environmental risk assessment of medicinal products for human use*. Doc. Ref. EMEA/CHMP/SWP/4447/00 corr 2.
- EU. (2020). Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption (recast) (Text with EEA relevance). *Official Journal of the European Union*, L 435, 23 December 2020, pp. 1–62.
- EurEau. (2017). *Europe's water in figures—An overview of the European drinking water and waste water sectors—2017 edition*. European Federation of National Associations of Water Services (EFNAWS). <http://www.eureau.org/resources/publications/1460-eureau-data-report-2017-1/file>
- Food & Agriculture Organization of the United Nations (FAO). (2000). Appendix 2. Parameters of pesticides that influence processes in the soil. In FAO Information Division Editorial Group (Ed.), *Pesticide Disposal Series 8. Assessing Soil Contamination. A Reference Manual*. <https://www.fao.org/3/x2570e/X2570E00.htm#TOC>
- Fox, P. M., Nico, P. S., Tfaily, M. M., Heckmann, K., & Davis, J. A. (2017). Characterization of natural organic matter in low carbon sediments: Extraction and analytical approaches. *Organic Geochemistry*, 114, 12–22.
- Franco, A., Ferranti, A., Davidsen, C., & Trapp, S. (2010). An unexpected challenge: Ionizable compounds in the REACH chemical space. *International Journal of Life Cycle Assessment*, 15, 321–325.
- Gellrich, V., Stahl, T., & Knepper, T. P. (2012). Behavior of perfluorinated compounds in soils during leaching experiments. *Chemosphere*, 87(9), 1052–1056.
- Green, V., & Karickhoff, S. W. (1990). Sorption estimates for modeling. In H. H. Cheng (Ed.), *Pesticides in the soil environment: Processes, impacts and modeling* (1st ed., pp. 79–101). Soil Science Society of America.
- Gustafson, D. (1989). Groundwater ubiquity score: A simple method for assessing pesticide leachability. *Environmental Toxicology and Chemistry*, 8(4), 339–357.
- Harrison, E. Z., Oakes, S. R., Hysell, M., & Hay, A. (2006). Organic chemicals in sewage sludges. *Science of the Total Environment*, 367(2–3), 481–497.
- Hartog, N., van Bergen, P. F., de Leeuw, J. W., & Griffioen, J. (2004). Reactivity of organic matter in aquifer sediments: Geological and geochemical controls. *Geochimica et Cosmochimica Acta*, 68(6), 1281–1292.
- Horwath, W. (2007). Chapter 12: Carbon cycling and formation of organic matter. In E. A. Paul (Ed.), *Soil microbiology, ecology, and biochemistry* (3rd ed., pp. 303–339). Academic Press.
- Jarvis, N. (2016). Extended sorption partitioning models for pesticide leaching risk assessments: Can we improve upon the Koc concept? *Science of the Total Environment*, 539, 294–303.
- Jobbágy, E. G., & Jackson, R. B. (2000). The vertical distribution of soil organic carbon and its relation to climate and vegetation. *Ecological Applications*, 10(2), 423–436.
- Kalberlah, F., Oltmanns, J., Schwarz, M., Baumeister, J., & Striffler, A. (2014). *Guidance for the precautionary protection of raw water destined for drinking water extraction from contaminants regulated under REACH*. Forschungs- und Beratungsinstitut Gefahrstoffe GmbH (FoBiG), denkbare GmbH.
- Karickhoff, S. W., Brown, D. S., & Scott, T. A. (1979). Sorption of hydrophobic pollutants on natural sediments. *Water Research*, 13(3), 241–248.
- Koskinen, W. C., & Harper, S. S. (1990). The retention process: Mechanisms. In H. H. Cheng (Ed.), *Pesticides in the soil environment: Processes, impacts and modeling* (1st ed., pp. 51–77). Soil Science Society of America.
- Kühne, R., Miltner, A., Kästner, M., Ost, N., Schäffer, A., & Schüürmann, G. (2016). *ECO24—Prediction of Non-Extractable Residues using structural information ('structural alerts')*. <http://cefic-iri.org/wp-content/uploads/2014/03/6.-Kuhne-ECO24-LRI-WS-2016.pdf>
- Lapworth, D. J., Lopez, B., Laabs, V., Kozel, R., Wolter, R., Ward, R., Vargas Amelin, E., Besien, T., Claessens, J., Delloye, F., Ferretti, E., & Grath, J. (2019). Developing a groundwater watch list for substances of emerging concern: A European perspective. *Environmental Research Letters*, 14(3), 035004. <https://doi.org/10.1088/1748-9326/aaf4d7>
- Lee, Y.-G., & Park, J.-H. (2013). Effect of soil organic carbon on sorption and desorption of perchloroethylene in soils. *Korean Journal of Chemical Engineering*, 30(2), 345–350.
- Li, Y., 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.
- Loeffler, D., Hatz, A., Albrecht, D., Fligg, M., Hogeback, J., & Ternes, T. A. (2020). Determination of non-extractable residues in soils: Towards a standardised approach. *Environmental Pollution*, 259, 113826.
- Manallack, D. T. (2009). The acid–base profile of a contemporary set of drugs: Implications for drug discovery. *SAR and QSAR in Environmental Research*, 20(7–8), 611–655. <https://doi.org/10.1080/10629360903438313>
- McCall, P. J., Laskowski, D. A., Swann, R. L., & Dishburger, H. J. (1981). Measurement of sorption coefficients of organic chemicals and their use, in environmental fate analysis. In *Test Protocols for Environmental Fate and Movement of Toxicants* (pp. 89–109). Proceedings of AOAC Symposium. AOAC.
- Mordaunt, C. J., Gevaio, B., Jones, K. C., & Semple, K. T. (2005). Formation of non-extractable pesticide residues: Observations on compound differences, measurement and regulatory issues. *Environmental Pollution*, 133(1), 25–34.
- Munira, S., Farenhorst, A., & Akinremi, W. (2018). Phosphate and glyphosate sorption in soils following long-term phosphate applications. *Geoderma*, 313, 146–153.
- Mylevaganam, S., & Ray, C. (2016). The assessment of groundwater vulnerability due to leaching of chemicals: The review of attenuation factor. *Open Journal of Soil Science*, 6, 9–20. <https://doi.org/10.4236/ojss.2016.61002>
- Neumann, M., & Schliebner, I. (2019). *Protecting the sources of our drinking water—The criteria for identifying Persistent, Mobile, and Toxic (PMT) substances and very Persistent, and very Mobile (vPvM) substances under EU REACH Regulation (EC) No 1907/2006*. German Environment Agency.
- Organisation for Economic Cooperation and Development (OECD). (2000). *Adsorption—Desorption using a batch equilibrium method*. OECD Guideline for the testing of chemicals No. 106.
- Organisation for Economic Cooperation and Development (OECD). (2001). *Estimation of the adsorption coefficient (K_{oc}) on soil and sewage sludge using high performance liquid chromatography (HPLC)*. OECD Guideline for the testing of chemicals No. 121.
- Organisation for Economic Cooperation and Development (OECD). (2002). *Aerobic and anaerobic transformation in soil*. OECD Guideline for the testing of chemicals No. 307.
- Organisation for Economic Cooperation and Development (OECD). (2004). *Leaching in soil columns*. OECD guidelines for the testing of chemicals, No. 312. <https://doi.org/10.1787/9789264070561-en>
- Panagos, P., Hiederer, R., Van Liedekerke, M., & Bampa, F. (2013). Estimating soil organic carbon in Europe based on data collected through an European network. *Ecological Indicators*, 24, 439–450.
- Payne, F. C., Quinnan, J. A., & Potter, S. T. (2008). *Remediation hydraulics*. CRC Press.
- Pignatello, J. J., & Xing, B. (1996). Mechanisms of slow sorption of organic chemicals to natural particles. *Environmental Science & Technology*, 30(1), 1–11. <https://doi.org/10.1021/es940683g>
- Piwoni, M. D., & Banerjee, P. (1989). Sorption of volatile organic solvents from aqueous solution onto subsurface solids. *Journal of Contaminant Hydrology*, 4(2), 163–179.

- Schäffer, A., Kästner, M., & Trapp, S. (2018). A unified approach for including non-extractable residues (NER) of chemicals and pesticides in the assessment of persistence. *Environmental Sciences Europe*, 30, 51. <https://doi.org/10.1186/s12302-018-0181-x>
- Schulze-Makuch, D. (2011). Groundwater: Advection, dispersion, sorption, degradation, attenuation. *Encyclopedia of life support systems* (Vol. II, p. 383).
- Sigmund, G., Arp, H. P. H., Aumeier, B. M., Bucheli, T. D., Chefetz, B., Chen, W., Droge, S. T. J., Endo, S., Escher, B. I., Hale, S. E., Hofmann, T., Pignatello, J., Reemtsma, T., Schmidt, T. C., Schönsee, C. D., & Scheringer, M. (2022). Sorption and mobility of charged organic compounds: How to confront and overcome limitations in their assessment. *Environmental Science and Technology*, 56(8), 4702–4710.
- Trapp, S., Brock, A. L., Kästner, M., Schäffer, A., & Hennecke, D. (2022). Critical evaluation of the microbial turnover to biomass approach for the estimation of biogenic non-extractable residues (NER). *Environmental Sciences Europe*, 34, 15. <https://doi.org/10.1186/s12302-022-00592-5>
- US Environmental Protection Agency (US EPA). (1996). *Soil screening guidance: User's guide* (2nd ed.). Office of Emergency and Remedial Response. EPA/540/R-96/018. NTIS PB96-963505.
- US Environmental Protection Agency (US EPA). (2003). *SCI-GROW description*. https://archive.epa.gov/oppefed1/web/html/scigrow_description.html
- US Environmental Protection Agency (US EPA). (2012). *Estimation Programs Interface Suite™ for Microsoft® Windows*, v 4.11.
- US Environmental Protection Agency (US EPA). (2020). *Series 835—Fate, transport and transformation test guidelines*. <https://www.epa.gov/test-guidelines-pesticides-and-toxic-substances/series-835-fate-transport-and-transformation-test>
- von Oepen, B., Kördel, W., Klein, W., & Schüürmann, G. (1991). Predictive QSPR models for estimating soil sorption coefficients: Potential and limitations based on dominating processes. *Science of the Total Environment*, 109–110, 343–354.
- Wauchope, R. D., Yeh, S., Linders, J. B. H. J., Kloskowski, R., Tanaka, K., Rubin, B., Katayama, A., Kördel, W., Gerstl, Z., Lane, M., & Unsworth, J. B. (2002). Pesticide soil sorption parameters: Theory, measurement, uses, limitations and reliability. *Pest Management Science*, 58(5), 419–445.
- Wendling, Z. A., Emerson, J. W., de Sherbinin, A., & Esty, D. C. (2020). 2020 *Environmental Performance Index*. Yale Center for Environmental Law & Policy. <https://doi.org/10.13140/RG.2.2.21182.51529>
- World Health Organization (WHO). (2017). *Guidelines for drinking-water quality: Fourth edition incorporating the first addendum*. <https://www.who.int/publications/i/item/9789241549950>
- World Health Organization (WHO). (2019). *National systems to support drinking-water, sanitation and hygiene: Global status report 2019*. UN-Water global analysis and assessment of sanitation and drinking-water (GLAAS) 2019 report. <https://www.who.int/publications/i/item/9789241516297>