Understanding requirements, limitations and applicability of QSAR and PTF models for predicting sorption of pollutants on soils: a systematic review

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Sorption is a key process to understand the environmental fate of pollutants on soils, conduct preliminary risk assessments and fill information gaps. Quantitative Structure-Activity Relationships (QSAR) and Pedotransfer Functions (PTF) are the most common approaches used in the literature to predict sorption. Both models use different outcomes and follow different simplification strategies to represent data. However, the impact of those differences on the interpretation of sorption trends and application of models for regulatory purposes is not well understood. We conducted a systematic review to contextualize the requirements for developing, interpreting, and applying predictive models in different scenarios of environmental concern by using pesticides as a globally relevant organic pollutant model. We found disagreements between predictive model assumptions and empirical information from the literature that affect their reliability and suitability. Additionally, we found that both model procedures are complementary and can improve each other by combining the data treatment and statistical validation applied in PTF and QSAR models, respectively. Our results expose how relevant the methodological and environmental conditions and the sources of variability studied experimentally are to connect the representational value of data with the applicability domain of predictive models for scientific and regulatory decisions. We propose a set of empirical correlations to unify the sorption mechanisms within the dataset with the selection of a proper kind of model, solving apparent incompatibilities between both models, and between model assumptions and empirical knowledge. The application of our proposal should improve the representativity and quality of predictive models by adding explicit conditions and requirements for data treatment, selection of outcomes and predictor variables (molecular descriptors *versus* soil properties, or both), and an expanded applicability domain for pollutant-soil interactions in specific environmental conditions, helping the decision-making process in regard to both scientific and regulatory concerns (in the following, the scientific and regulatory dimensions).

KEYWORDS

environmental fate, organic pollutants, pesticides, decision-making, model interpretation

1 Introduction

Sorption is a key process in tracking the environmental fate of pollutants on soils due to its role in increasing the persistence and accumulation (Dollinger et al., 2015; Rybacka and Andersson, 2016; Zhu et al., 2017; De Gerónimo et al., 2018; Cai et al., 2019; Conde-Cid et al., 2019; Pandey and Roy, 2021) by reducing their transport (Kodešová et al., 2015; Wang et al., 2015; Sidoli et al., 2016; De Gerónimo et al., 2018; Zhang et al., 2018; Cai et al., 2019; Conde-Cid et al., 2019; Conde-Cid et al., 2020; Pandey and Roy, 2021; Hu et al., 2022) and bioavailability (Kodešová et al., 2015; Zhang et al., 2018; Cai et al., 2019; Conde-Cid et al., 2020; Cantwell et al., 2022; Hu et al., 2022), and negatively affecting their biodegradation (Dollinger et al., 2015; Aranda et al., 2016; Zhang et al., 2018; Cai et al., 2019; Pandey and Roy, 2021; Cantwell et al., 2022) and bioremediation (Cantwell et al., 2022). This has led to the development of various models for the prediction of sorption, with two taking a dominant position in the literature: quantitative structure-activity relationships (QSAR) and pedotransfer functions (PTF). Both models are considered an efficient option for conducting preliminary risk assessment, filling information gaps, identify soil issues and guide soil management and sustainability in different soils of interest (e.g., agricultural, polluted, and vulnerable soils) when the production of experimental data may be infeasible for real time and large-scale decision-making (Wang et al., 2015; Aranda et al., 2016; Sidoli et al., 2016; Singh et al., 2016; Berthod et al., 2017; Sabour and Moftakhari Anasori Movahed, 2017; Zhu et al., 2017; De Gerónimo et al., 2018; Zhang et al., 2018; Cai et al., 2019; Conde-Cid et al., 2019; Conde-Cid et al., 2020; Kobayashi et al., 2020; Kobayashi and Yoshida, 2021; Muhire et al., 2021; Pandey and Roy, 2021; Cantwell et al., 2022; Hu et al., 2022; Jiang et al., 2022). Additionally, both models predict sorption on soils through sorption coefficients, which represent the linear/nonlinear distribution between the retained and the aqueous concentration of pollutant in chemical equilibrium in sorption isotherm studies (Neira-Albornoz et al., 2022).

Despite the fact that both kinds of models seem applicable under similar conditions and have been scientifically validated in their predictive ability, their shared goal is pursued by employing different procedures and assumptions that entail different chemical, computational, and regulatory implications. We therefore identified three factors that may affect their reliability and suitability for regulatory purposes: (i) outcome selection, which depends on the experimental design and conditions as well as methodological considerations due to the complexity of environmental systems (Neira-Albornoz et al., 2022); (ii) simplification strategy, with QSAR models describing the sorption process through molecular properties of pollutants (Wang et al., 2015; Aranda et al., 2016; Berthod et al., 2017; Sabour and Moftakhari Anasori Movahed, 2017; Zhu et al., 2017; Zhang et al., 2018; Cai et al., 2019; Kobayashi et al., 2020; Kobayashi and Yoshida, 2021; Muhire et al., 2021; Pandey and Roy, 2021; Cantwell et al., 2022; Jiang et al., 2022), and PTF assuming that the sorption depends on the local soil properties instead (Sidoli et al., 2016; Singh et al., 2016; De Gerónimo et al., 2018; Conde-Cid et al., 2019; Conde-Cid et al., 2020; Hu et al., 2022); and (iii) institutionalization, where only QSAR models have been promoted by the Organization for Economic Co-operation and Development (OECD), the Registration,

Evaluation, Authorization, and Restriction of Chemicals (REACH) and the U.S. Environmental Protection Agency (USEPA), based on institutional requirements and guidelines (OECD, 2014; Card et al., 2017; Kar et al., 2018; Thomas et al., 2019; Chinen and Malloy, 2020).

For instance, different, non-equivalent sorption coefficients are used to represent the sorption process (Mamy et al., 2015; Nolte and Ragas, 2017; Neira-Albornoz et al., 2022), which are interpreted as physicochemical properties of pollutants (QSAR) or of soils (PTF), affecting the data collection, data treatment and the reliability, comparability, and applicability of their predictions in real scenarios. Therefore, understanding the background of QSAR and PTF models is crucial to determine when and how to apply them in environmental contexts of concern. However, this comparative background is not fully understood, creating uncertainty in both scientific and decision-making practice.

In this work, we assess the links between the underlying assumptions of predictive models and the state-of-the-art based on experimental studies to develop a conceptual background for improving the use of models for the prediction of the sorption of pollutants on soils for regulatory purposes. We contribute to the scientific practice and decision-making processes in three ways: (i) we develop a comprehensive analysis of two contrasting approaches for predicting sorption coefficients for regulatory purposes, (ii) we connect the QSAR and PTF theories to current experimental trends, and (iii) we propose a procedure that unifies and improves the contextualization and interpretability of predictive models.

2 Methodology

Our methodology included three stages: (i) the presentation of an explicit scope to introduce our audience and contextualize the outcomes and pollutants assessed in our study, (ii) the description of the systematic review, and (iii) the extraction of information from the literature. We divided the last step into (i) QSAR and PTF models to describe and compare their development backgrounds, and (ii) empirical findings from the literature to contrast them with the development and interpretation of predictive models.

2.1 Scope of the study

2.1.1 Sorption coefficients
Our study is focused on three sorption coefficients used as outcomes in QSAR and PFT models to describe the sorption of pollutants of environmental concern: (i) the linear coefficient, K_d, (ii) the nonlinear Freundlich coefficient, K_F, whose interpretation depends on the degree of curvature of the sorption isotherm, described through a linearity coefficient, $1/n$, and (iii) the soil organic carbon-normalized sorption coefficient, K_{OC}, quantified from K_d or K_F when soil organic carbon content (OC) is the dominant sorbent in soils.

2.1.2 Approach
Our analysis involved three layers (Engeström, 2011; Jensen, 2022): (i) an interpretative layer, where assumptions used by scientists and predictive models to make decisions were explicitly defined and addressed, (ii) a contradictory layer, where contradictions among QSAR and PTF assumptions were

FIGURE 1
Representation of the decision-making process used in this study.
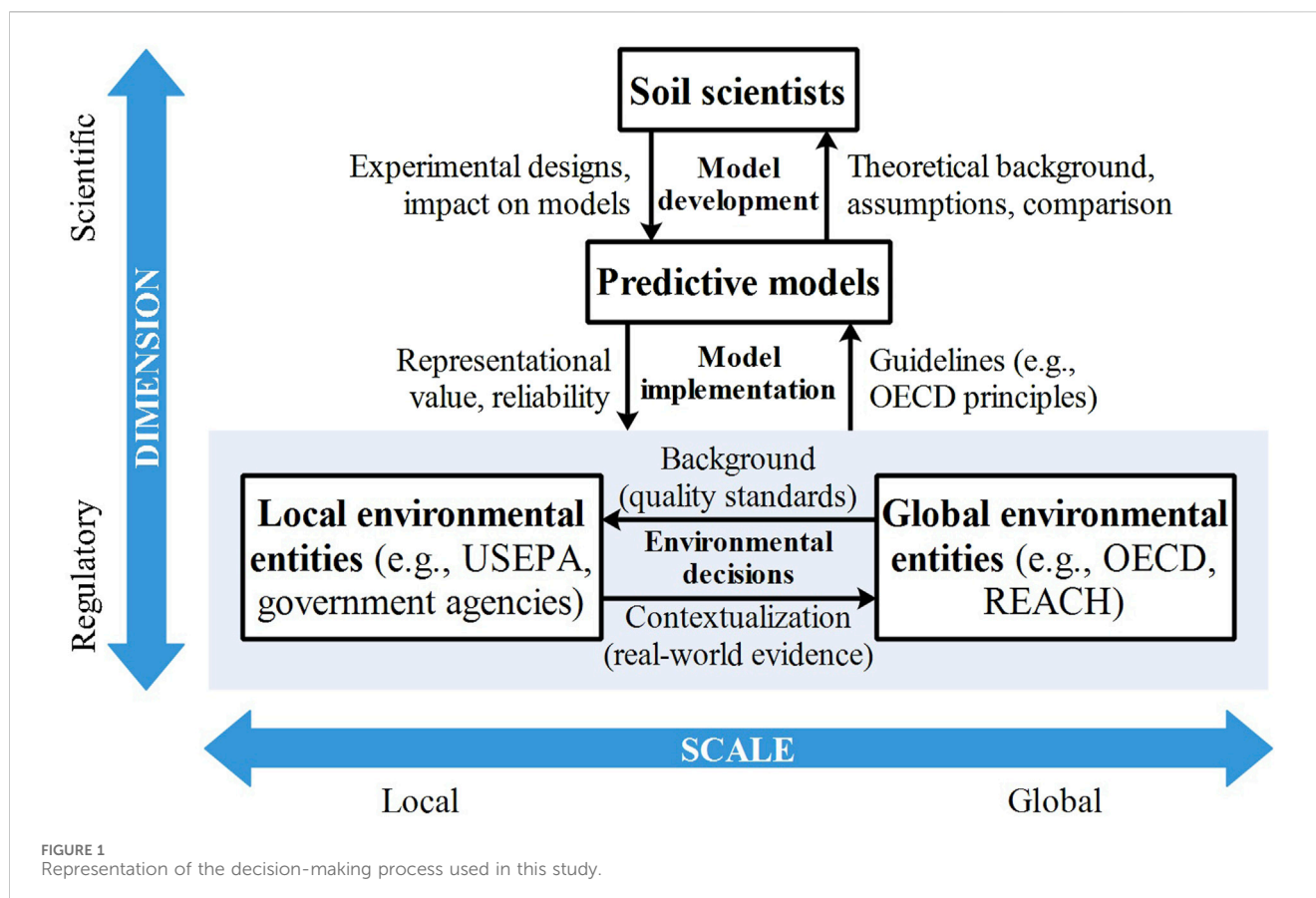
analyzed, and (iii) an agentive layer, involving different actors that transform scientific practices, including regulatory agencies (e.g., OECD guidelines for the development of predictive models) (OECD, 2014).

The interpretative layer has already been addressed in critical reviews for QSAR (Hansen et al., 1999; Mamy et al., 2015; Nolte and Ragas, 2017) and PTF (McBratney et al., 2002; Van Looy et al., 2017) models, independently. However, they were not contrasted with each other (QSAR vs. PTF) nor with experimental studies. In this article, we compared both models and included three scientific actors (QSAR developers, PTF developers, and soil scientists conducting experimental research), their assumptions as well as potential contradictions, and the impact of OECD guidelines on the scientific practices.

2.1.3 Decision-making process

We defined two dimensions: scientific and regulatory (Figure 1). The scientific dimension is composed of soil scientists who conduct experimental research or develop and use predictive models (scientific decisions). The regulatory dimension involves environmental entities that apply those models in different socio-environmental contexts at local or global scale (regulatory decisions).

Our study considers scientific decisions as model development, where the interpretative layer consist of (i) experimental designs used by soil scientists to produce data, and (ii) theoretical background and assumptions applied during the predictive model development. Additionally, a contradictory layer was addressed through the comparison of (i) QSAR and PTF models, and (ii) predictive models *versus* empirical information.

In addition, we considered regulatory decisions as model implementation through a contradictory layer that considered the concord between experimental designs and predictive model assumptions to evaluate the representational value of data and reliability of predictions. In addition, we included an agentive layer based on the OECD principles (OECD, 2014), which are used in QSAR models and equivalent to some REACH conditions (Chinen and Malloy, 2020).

In this sense, our approach (Figure 1) shows how different scientific and regulatory decisions are mediated by predictive models that act as an interface (e.g., science-policy interaction) and whose understanding requires a holistic approach.

2.2 Systematic literature review

As the basis for our investigation, we conducted two systematic literature reviews about research into the sorption of organic pollutants on soils: one for QSAR and PTF models (Figure 2A) and another for experimental sorption studies (Figure 2B).

Based on the number of published articles, we used two intervals of recent years to represent research and trends conducted with comparable and currently validated procedures: 5 years (2017–2021) for experimental studies, and (ii) 8 years (2015–2022) for QSAR and PTF models.

We identified numerous experimental studies, which exceeded the feasible amount for manual annotation, and consequently selected pesticides as a globally relevant organic pollutant model

FIGURE 2
Flow chart and procedure for the analysis of recent articles that **(A)** develop predictive models, and **(B)** conduct experimental studies.
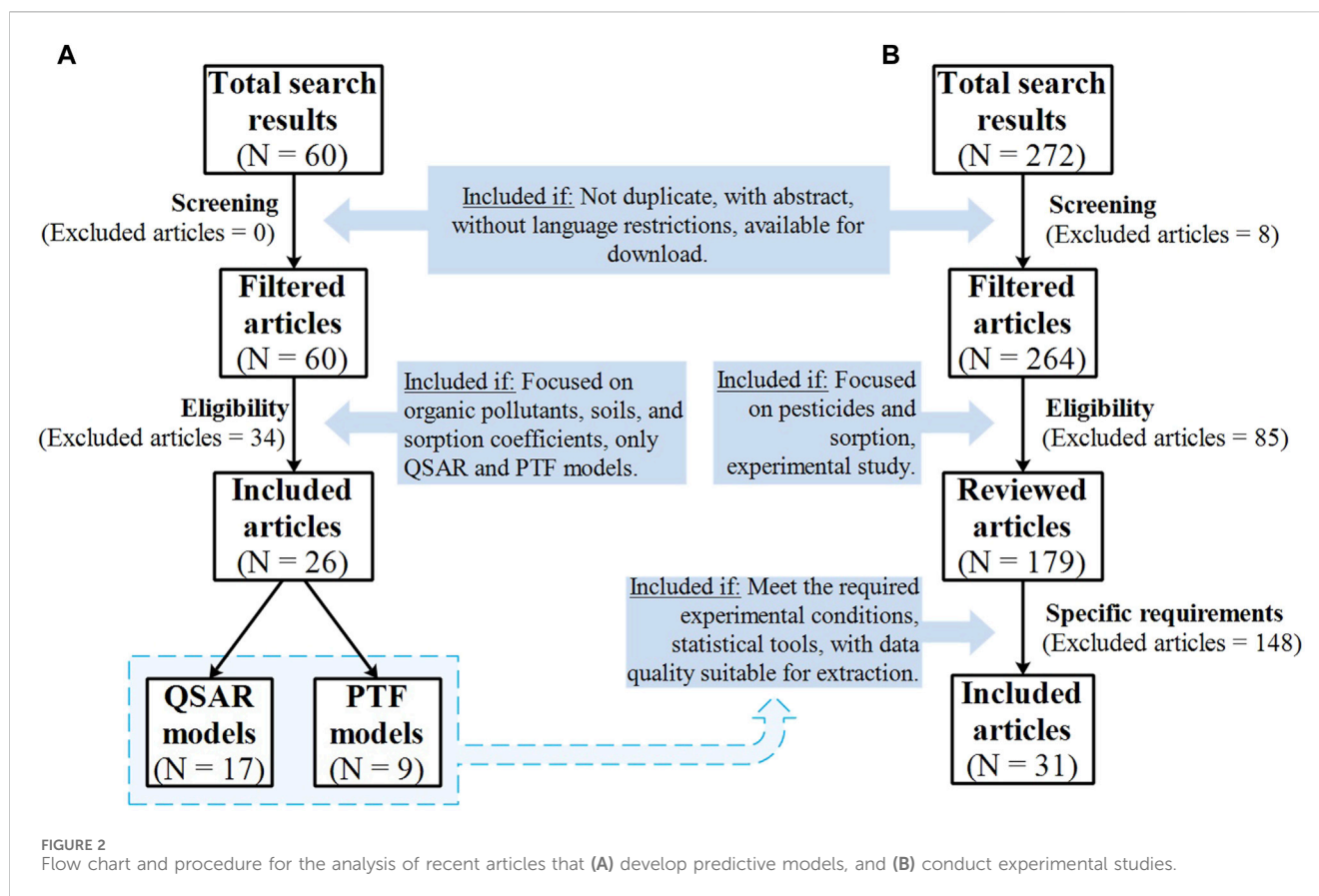
of focus. While reducing the manual data extraction to a scope that was feasible to conduct, this also ensured a sufficiently diverse number of pollutants in the considered studies, allowing us to extrapolate our findings to other organic pollutants assessed by QSAR and PTF models.

A schematic overview is shown in Figure 2. A detailed description of our search strategy (keywords, search date, dataset used) and the application of inclusion criteria for each individual article are listed in Supplementary Table S1 for QSAR and PTF models, and Supplementary Table S2 for experimental sorption studies. In screening the related work, we discarded duplicates, articles without abstract, with language restrictions, or those that were not downloadable. We then applied eligibility criteria for each literature review. For predictive models, we included articles focused on QSAR or PTF models to predict sorption coefficients of organic pollutants on soils, describing their procedure (Figure 2A; Supplementary Table S1). For experimental studies, we included articles conducting experimental studies on the sorption of pesticides on soils and soil-related sorbents (Figure 2B; Supplementary Table S2).
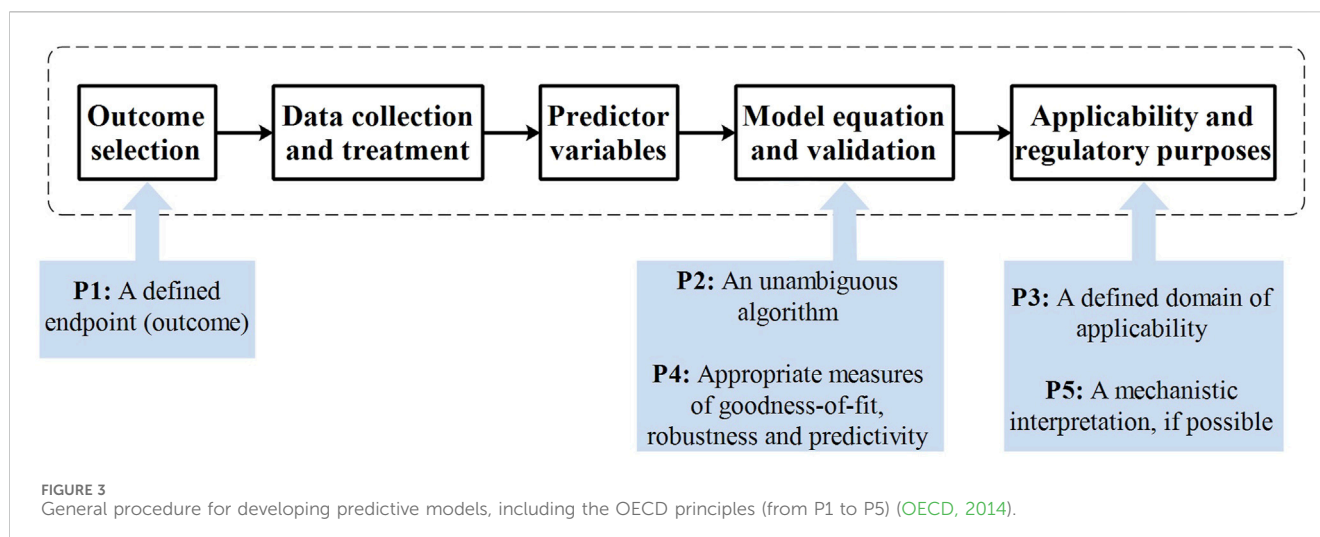
We only included experimental studies that meet three specific requirements based on the selected predictive models (Figure 2B; Supplementary Table S2). First, experimental conditions that ensure data comparability and representativeness: the corroboration of equilibrium condition through kinetic studies, mention of the isotherm shape, and description of the quantification method (e.g., mass balance to quantify the sorbed concentration from the aqueous concentration). Second, the use of statistical tools to

validate sorption coefficients: Pearson coefficient >0.95 and five or more concentration points to produce one sorption coefficient, based on the minimum observation:descriptor ratio proposed for QSAR models to avoid overfitting (Roy et al., 2015). Finally, the suitability and comprehensiveness of the provided data descriptions for data extraction: an explicit calculation of sorption coefficients including clear values, units and nomenclature along the article, and explicit conditions where data were quantified, such as solution, sorbent:solution ratio, and interval of concentrations.

All selection criteria were applied successively.

2.3 Description of QSAR and PTF development procedures

We conducted a descriptive analysis of scientific articles producing predictive models through the following process: First, we divided their procedures into shared steps (Figure 3). Then, we extracted information related to each step: outcome selection (outcome, units, accomplishment of the OECD principle P1), data collection and treatment (data production, data mining, diversity of data, experimental conditions used to quantify data within the dataset, data treatment, kind of sorption coefficients included in the dataset), predictor variables (kind of predictor, quantification method), model equation and validation (splitting procedures, algorithms linked to the OECD principles P2 and P4), and applicability and regulatory purposes (considering the OECD principles P3 and P5). This information is shown in

FIGURE 3
General procedure for developing predictive models, including the OECD principles (from P1 to P5) (OECD, 2014).

Supplementary Table S3. Later, we compared the approaches both models followed, and finally we identified and described similarities and differences, summarizing relevant patterns for the development of predictive models.

Additionally, we proposed QSAR and PTF assumptions for explaining common procedures during the model development procedures. Assumptions are (i) implicit within each article, (ii) derived from general observations during the development of predictive models, and (iii) conceptually linked to the simplification strategies followed by both predictive models.

2.4 Extraction and classification of the empirical information

The following information was extracted from the experimental studies (Figure 2B): (i) data per article, (ii) sources of variability explored during the experimental design within each article, (iii) pesticides studied per article (to evaluate frequency and consistency among studies), and (iv) characterization of pesticides studied within an article by name, target, acid-base activity, and chemical class.

The information extracted from articles is shown in Supplementary Table S4, where we classified the sources of variability addressed within each article into two groups: soil variability (SV) and other sources of variability (OV). SV included the use of different soils (SV [soil]), treatments applied to the soils prior to the experiment (SV [treat]), spatial variability during the soil sampling process (SV [spatial]), and the lack of soil variability (SV [none]). On the other hand, OV included the use of different pesticides (OV [pollut]), control and analysis of specific experimental conditions (OV [exp]), and the lack of other sources of variability (OV [none]). The effect of time (OV [time]) was investigated in a few reviewed articles and discarded during the application of specific requirements for the included articles (Figure 2B).

During the classification of soil variability, we considered soil-related sorbents (e.g., soils, sediments, microplastics) as independent. Additionally, we defined SV [treat] as treatments made to one soil that modifies its structural composition, such as additions (e.g., application of organic amendments, biochar at one or different temperatures, lime, fertilizers, adjuvants, microplastics),

removals (e.g., removal of organic matter), isolation of components (e.g., extraction of clay fractions), and management practices. In this sense, different sorbents obtained from one soil were considered as SV [treat] instead of SV [soil]. Finally, SV [spatial] encodes topographic variations in which all samples belong to the same soil but at different depths, horizons, or surface location in one plot.

For other sources of variability, OV [pollut] represents the quantification of the sorption coefficient of different chemicals in the same article, while OV [exp] represents the application of different approaches to describe the behavior of the same pollutant, such as sorption studies (e.g., one-point and sorption isotherm), experimental conditions (e.g., pure pesticides, mixture of pesticides, commercial formulations) and control of variables (e.g., the effect of temperature, pH, salinity, soil solution composition and sterilization of soils in the sorption experiment).

Pesticide names were homogenized when the same pesticide had different names among the articles, and their attributes were derived from the Pesticide Properties Database, PPDB (Lewis et al., 2016). Then, the most relevant functional groups of every pesticide were obtained from the database (Lewis et al., 2016). The groups were ordered according to the number of apparitions among the studies, and pesticides were successively classified considering their most frequent group. The compounds with low-frequent groups or lack of information on the PPDB website were classified within the groups in which they fit the best after a structural analysis. Finally, we created four sub-groups according to common characteristics within the groups, whose chemical structures are shown in Supplementary Figure S1. The information about pesticides is shown in Supplementary Table S5.

The combination of articles studying the same pesticide was used to evaluate (i) sources of variability available in the literature per pesticide, (ii) number of articles studying a pesticide, and (iii) characterization of individual pesticides. Then, the distribution of information was analyzed among articles and pesticides, and the contrast with QSAR and PTF assumptions and the impact for scientific and regulatory decisions was discussed.

Finally, we analyzed the interpretation of current QSAR models through the following procedure: (i) we considered the averaged sorption coefficient values for one pesticide among different soils

TABLE 1 Summary of the information extracted from QSAR and PTF models from the literature (presented in the same order as in Supplementary Table S3).

#	Article Ref.	Outcome (units)[a]	Data included in the dataset Type[b]	Diversity[c]	Predictive model development Predictor (quantification)[d]	Splitting[e]	Model equation (validation methods)[f]	Applicability domain
QSAR models								
1	Cantwell et al. (2022)	log K_{OC} (Not shown)	T	**P:** 21 PBDEs. **S:** unclear. **Data:** (21 × 1 = 21)	Mol (sof)	TTS	Yes (GoF, Rob, PrA)	Not included
2	Jiang et al. (2022)	log K_{OC} (Not shown)	T and E (lit)	**P:** 22 PFAs. **S:** Sediments and soils. **Data:** (22 × 1 = 22)	Mol (sof)	TTS	Yes (GoF, Rob, PrA)	Yes
3	Muhire et al. (2021)	log K_{OC} (Not shown)	T	**P:** 24 OPI. **S:** unclear. **Data:** (24 × 1 = 24)	Mol (sof)	TTS	Yes (GoF, Rob, PrA)	Yes
4	Kobayashi and Yoshida (2021)	log K_{OC} (Not shown)	E (lit)	**P:** 964 NIOC. **S:** unclear. **Data:** (964 × 1 = 964)	Mol (sof)	TTS	Yes (GoF, Rob, PrA)	Yes
5	Pandey and Roy (2021)	log K_{OC} (Not shown)	E (lit)	**P:** 223 OrC. **S:** unclear. **Data:** (223 × 1 = 223)	Mol (sof)	TTS, PCPCs	Yes (GoF, Rob, PrA)	Yes
6	Kobayashi et al. (2020)	log K_{OC} (Not shown)	E (lit)	**P:** 163 Pes. **S:** unclear. **Data:** (163 × 1 = 163)	Mol (sof)	TTS	Yes (GoF, Rob)	Yes
7	Cai et al. (2019)	log K_{OC} (Not shown)	E (lit)	**P:** 27 PAHs and PAEs. **S:** unclear. **Data:** (27 × 1 = 27)	Mol (sof)	TTS	Yes (GoF, Rob, PrA)	Yes
8	Olguin et al. (2019)	log K_{OC} (Not shown)	E (lit)	**P:** 964 NIOC. **S:** unclear. **Data:** (964 × 1 = 964)	Mol (sof)	TTS	Yes (GoF, Rob, PrA)	Yes
9	Zhang et al. (2018)	log K_{OC} (Not shown)	E (lit)	**P:** 60 PMeODEs, PHODEs, PCDEs. **S:** unclear. **Data:** (60 × 1 = 60)	Mol (sof)	TTS, PCPCs	Yes (GoF, Rob, PrA)	Yes
10	Daré et al. (2017)	log K_{OC} (Not shown)	T	**P:** 24 OPI. **S:** unclear. **Data:** (24 × 1 = 24)	Mol (sof)	TTS	Yes (GoF, Rob, PrA)	Yes
11	Olguin et al. (2017)	log K_{OC} (Not shown)	E (lit)	**P:** 964 NIOC. **S:** unclear. **Data:** (964 × 1 = 964)	Mol (sof)	TTS	Yes (GoF, Rob, PrA)	Not included
12	Sabour and Moftakhari Anasori Movahed (2017)	log K_{OC} (Not shown)	Mostly T	**P:** 800 OrC. **S:** unclear. **Data:** (800 × 1 = 800)	Mol (sof)	TTS	Yes (GoF, Rob, PrA)	Yes

TABLE 1 (*Continued*) Summary of the information extracted from QSAR and PTF models from the literature (presented in the same order as in Supplementary Table S3).

	Article	Outcome (units)[a]	Data included in the dataset		Predictive model development			Applicability domain
#	Ref.		Type[b]	Diversity[c]	Predictor (quantification)[d]	Splitting[e]	Model equation (validation methods)[f]	
QSAR models								
13	Berthod et al. (2017)	log K_d (L kg^{-1})	E (lit)	**P:** 148 Pha and major metabolites. **S:** unclear. **Data:** (148x [>1] = 297)	Mol (sof)	TTS, PCPCs	Yes (GoF, Rob, PrA)	Not included
14	Zhu et al. (2017)	log K_{OC}^{op} (Not shown)	E (lit)	**P:** 52 PCBs. **S:** One specific soil **Data:** (52 × 1 = 52)	Mol (sof)	TTS	Yes (GoF, Rob, PrA)	Yes
15	Rybacka and Andersson (2016)	log K_d (L kg^{-1})	E (lit)	**P:** 110 Pha. **S:** Sewage sludges **Data:** (110 × 1 = 110)	Mol (sof)	TTS, PCPCs	Yes (PrA in the training set)	Not included
16	Aranda et al. (2016)	log K_{OC} (Not shown)	E (lit)	**P:** 643 OrC. **S:** unclear. **Data:** (643 × 1 = 643)	Mol (sof)	TTS	Yes (GoF, Rob, PrA)	Yes
17	Wang et al. (2015)	log K_{OC} (L kg^{-1})	T and E (lit)	**P:** 824 OrC. **S:** unclear. **Data:** (824 × 1 = 824)	Mol (sof)	TTS	Yes (GoF, Rob, PrA)	Yes
PTF models								
1	Hu et al. (2022)	**1.** K_d (L kg^{-1}) **2.** K_F (mg$^{1-1/n}$ L$^{1/n}$ kg^{-1})	E (lit)	**P:** 7 ABs. **S:** 79–159 soils. **Data:** (7x [79-159] = 694)	SP and MC (exp)	TTS, comp	Yes (GoF, PrA)	No (but an alternative analysis was made)
2	Conde-Cid et al. (2020)	K_F (L^n µmol^{1-n} kg^{-1})	E (exp)	**P:** 2 ABs **S:** 63 agricultural soils. **Data:** (2 × 63 = 126)	SP (exp)	Comp	Yes (GoF)	Not included
3	Conde-Cid et al. (2019)	**1.** K_d (L kg^{-1}) **2.** K_F (L$^{1/n}$ µmol$^{1-1/n}$ kg^{-1})	E (exp)	**P:** Sulfadiazine. **S:** 68 agricultural soil samples. **Data:** (1 × 68 = 68)	SP (exp)	TTS, soil	Yes (GoF)	Not included
4	De Gerónimo et al. (2018)	K_F ((mg kg^{-1}) (mg L^{-1}))	E (exp)	**P:** Glyphosate. **S:** 12 soils. **Data:** (1 × 12 = 12)	SP (unclear)	Not applied	Yes (GoF, Rob)	Not included
5	Klement et al. (2018)	K_F (cm$^{3/n}$ µg$^{1-1/n}$ g^{-1})	E (exp)	**P:** 3 Pha. **S:** 7 soils. **Data:** (3 × 7 = 21)	SP (exp)	Comp	Yes (GoF)	Not included
6	Singh et al. (2016)	K_d^{op} (L kg^{-1})	E (exp)	**P:** 2,4-D and atrazine. **S:** 591 soil samples. **Data:** (2 × 591 > 1,000)	SP (unclear)	TTS, comp, soil	Yes (GoF, PrA)	Not included

TABLE 1 (*Continued*) Summary of the information extracted from QSAR and PTF models from the literature (presented in the same order as in Supplementary Table S3).

	Article	Outcome (units)[a]	Data included in the dataset		Predictive model development			Applicability domain
#	Ref.		Type[b]	Diversity[c]	Predictor (quantification)[d]	Splitting[e]	Model equation (validation methods)[f]	
PTF models								
7	Sidoli et al. (2016)	K_f ((mg kg^{-1}) (L mg^{-1})$^{-1/n}$)	E (exp)	**P:** Glyphosate and AMPA. **S:** 15 agricultural soils. **Data:** (2 × 15 = 30)	SP (exp)	Comp	Yes (GoF)	Not included
8	Dollinger et al. (2015)	1. K_f (L kg^{-1} 1/n^{-1}) 2. K_d^{op} (Not shown) 3. 1/n (dimensionless)	E (lit)	**P:** Glyphosate. **S:** 101 soils and sediments **Data:** (1 × 101 = 101)	SP (unclear) and MC (exp)	Sorp	Yes (GoF, Rob)	No (but an alternative analysis was made)
9	Kodešová et al. (2015)	K_F (cm$^{3/n}$ µg$^{1-1/n}$ g^{-1})	E (exp)	**P:** 7 Pha. **S:** 13 soils. **Data:** (7 × 13 = 91)	SP (exp)	Comp	Yes (GoF)	No (but an alternative analysis was made)

[a]Note that (i) some units are not shown (e.g., QSAR models) or are incorrectly defined (e.g., K_F for PTF 8), (ii) it is unclear the origin of K_{OC} when used, and (iii) we included the superscript "op" for outcomes that were quantified from one specific initial concentration of pollutant (one-point K_d or K_{OC}) instead of a sorption isotherm.

[b]**T:** theoretical (predicted), **E(lit):** empirical (from literature), **E(exp):** empirical (quantified in this study).

[c]Two categories were used, i.e., **P:** pollutants, **S:** Sorbents. Additionally, some P were abbreviated, i.e., **ABs:** antibiotics, **NIOC:** non-ionic organic compounds, **OrC:** organic chemicals, **OPI:** organophosphorus insecticides, **PAEs:** phthalic acid esters, **PAHs:** polycyclic aromatic hydrocarbons, **PBDEs:** polybrominated diphenyl ethers, **PCBs:** polychlorinated biphenyl congeners, **PCDEs:** Hydroxylated- and methoxylated-polychlorinated diphenyl ethers, **Pes:** pesticides, **PFAs:** perfluorinated and polyfluoroalkyl substances, **Pha:** pharmaceuticals, **PHODEs:** polyhydroxylated diphenyl ethers, **PMeODEs:** polymethoxylated diphenyl ethers.

[d]Three kinds of descriptors, i.e., **Mol:** molecular descriptors, **SP:** soil properties, **MC:** methodological conditions. Two kinds of quantification were abbreviated, i.e., **Sof:** software, **Exp:** experimental.

[e]**Comp:** one model per compound, **PCPCs:** classification by physicochemical properties of compounds, i.e., chemical classes or charge state, **Soil:** One model per soil, **Sorp:** Classification by sorption characteristics, i.e., experimental information or sorption trend, **TTS:** Use of training:test sets.

[f]**GoF:** Goodness-of-fit, **PrA:** predictive ability, **Rob:** Robustness.

(called $K_{F(pest)}$ and $K_{OC(pest)}$), and for one soil among different pesticides (called $K_{F(soil)}$ and $K_{OC(soil)}$), then (ii) we quantified the coefficients of variation (COV) for $K_{F(pest)}$ and $K_{F(soil)}$, and lastly (iii) we contrasted the COV for $K_{F(pest)}$ and $K_{OC(pest)}$ (related to SV [soil]) with $K_{F(soil)}$ and $K_{OC(soil)}$ (related to OV [pollut]).

3 Literature review results

In this section we present our results for predictive models and empirical findings. Table 1 is a condensed version of Supplementary Table S3 and acts as a guide for reader in this section, showing information from Figure 3 for each article, such as outcome, data collection and treatment (type and diversity), predictor variables, model equation and validation, and applicability domain.

3.1 Literature on predictive model development

Based on the articles found in the literature (17 QSAR and 9 PTF models, Figure 2A), we provide a comprehensive analysis by considering the key development steps of QSAR and PTF models

(Figure 3). Furthermore, we include the five principles proposed by the OECD to guide the development procedure of QSAR models for regulatory purposes (P1-5, Figure 3) (OECD, 2014), to enable a comparison between QSAR and PTF models.

3.1.1 Outcome selection
3.1.1.1 QSAR models

According to the QSAR model theory, activities or properties of pollutants (e.g., sorption coefficients) are explained by their chemical structure (Aranda et al., 2016; Olguin et al., 2019). This implies that the outcome is exclusively dependent on pollutants, or put another way, independent of soil properties.

In the literature, a high correlation between soil organic carbon content (OC) and sorption coefficients has been found for non-ionizable or neutral pollutants sorbed on soils with OC > 0.1% (Olguin et al., 2017; Olguin et al., 2019). This minimizes the soil variability (only OC is important) and allows the extrapolation of trends to other soils having the same sorption mechanism, especially if the mechanism is unspecific (i.e., pollutants may interact with different types of sorption sites) and generalizable (i.e., a specific soil component may represent the whole sorption), such as hydrophobic. Under this scenario, the sorption coefficient is a property of pollutants (Olguin et al., 2017; Cai et al., 2019).

In this sense, most QSAR models predicted K_{OC} (Wang et al., 2015; Aranda et al., 2016; Olguin et al., 2017; Sabour and Moftakhari Anasori Movahed, 2017; Zhu et al., 2017; Zhang et al., 2018; Cai et al., 2019; Olguin et al., 2019; Kobayashi et al., 2020; Kobayashi and Yoshida, 2021; Muhire et al., 2021; Pandey and Roy, 2021; Cantwell et al., 2022; Jiang et al., 2022) of non-ionizable and neutral compounds, such as diphenyl ethers and biphenyl congeners (Zhu et al., 2017; Zhang et al., 2018; Cantwell et al., 2022), perfluorinated and polyfluoroalkyl substances (Jiang et al., 2022), polycyclic aromatic hydrocarbons and phthalic acid esters (Cai et al., 2019), pharmaceuticals (Rybacka and Andersson, 2016; Berthod et al., 2017), pesticides (Kobayashi et al., 2020), organophosphorus insecticides (Daré et al., 2017; Muhire et al., 2021), or several organic compounds of different chemical classes (Wang et al., 2015; Olguin et al., 2017; Sabour and Moftakhari Anasori Movahed, 2017; Olguin et al., 2019; Kobayashi and Yoshida, 2021; Pandey and Roy, 2021).

3.1.1.2 PTF models

In contrast to QSAR, PTF theory considers that correlational associations among soil properties have explanatory implications for other soil properties (Sidoli et al., 2016; Singh et al., 2016; De Gerónimo et al., 2018; Conde-Cid et al., 2020). Therefore, sorption coefficients of one pollutant among different soils must depend on soil properties.

In the literature, different sorption mechanisms and trends have been found for the same pollutant, e.g., a major and a minor role of OC in the sorption of oxytetracycline and chlortetracycline across different soils (Conde-Cid et al., 2020) or non-hydrophobic sorption mechanisms (Dollinger et al., 2015; Kodešová et al., 2015; Sidoli et al., 2016; De Gerónimo et al., 2018; Klement et al., 2018), in accordance with the PTF theory.

Additionally, the outcome selection process was linked to the evaluation of sorption linearity during the data treatment (Kodešová et al., 2015; Sidoli et al., 2016; Klement et al., 2018) and the analysis of predictor variables related to the environmental and methodological conditions, such as tillage (Singh et al., 2016) or the presence of phosphate (Sidoli et al., 2016) in agricultural soils.

In this sense, PTF models studied one pollutant at a time, including pesticides (Dollinger et al., 2015; Sidoli et al., 2016; Singh et al., 2016; De Gerónimo et al., 2018), pharmaceuticals (Kodešová et al., 2015; Klement et al., 2018), and antibiotics (Conde-Cid et al., 2019; Conde-Cid et al., 2020; Hu et al., 2022), generally ionizable (Dollinger et al., 2015; Kodešová et al., 2015; Sidoli et al., 2016; De Gerónimo et al., 2018; Klement et al., 2018; Conde-Cid et al., 2019; Conde-Cid et al., 2020; Hu et al., 2022), and using non-normalized sorption coefficients (K_d and K_F) (Dollinger et al., 2015; Kodešová et al., 2015; Sidoli et al., 2016; Singh et al., 2016; De Gerónimo et al., 2018; Klement et al., 2018; Conde-Cid et al., 2019; Conde-Cid et al., 2020; Hu et al., 2022) and sorption isotherm linearity (Dollinger et al., 2015) for representing the linear (1/n = 1) and nonlinear (1/n ≠ 1) sorption under specific conditions.

3.1.1.3 Key insights

We found different strategies that were employed to simplify the sorption process. QSAR models considered the sorption coefficient as a physicochemical property of pollutants, independent of soils and are therefore valid for all soils, simplifying the outcome selection (P1, Figure 3). PTF models evaluated one pollutant per model,

considering that the sorption coefficient is a soil property. This implies that QSAR models, when applicable, are broad and general, while PTF models tend to be specific, acquiring local relevance. Figure 4 shows conditions and assumptions that we propose to understand both kinds of predictive models.

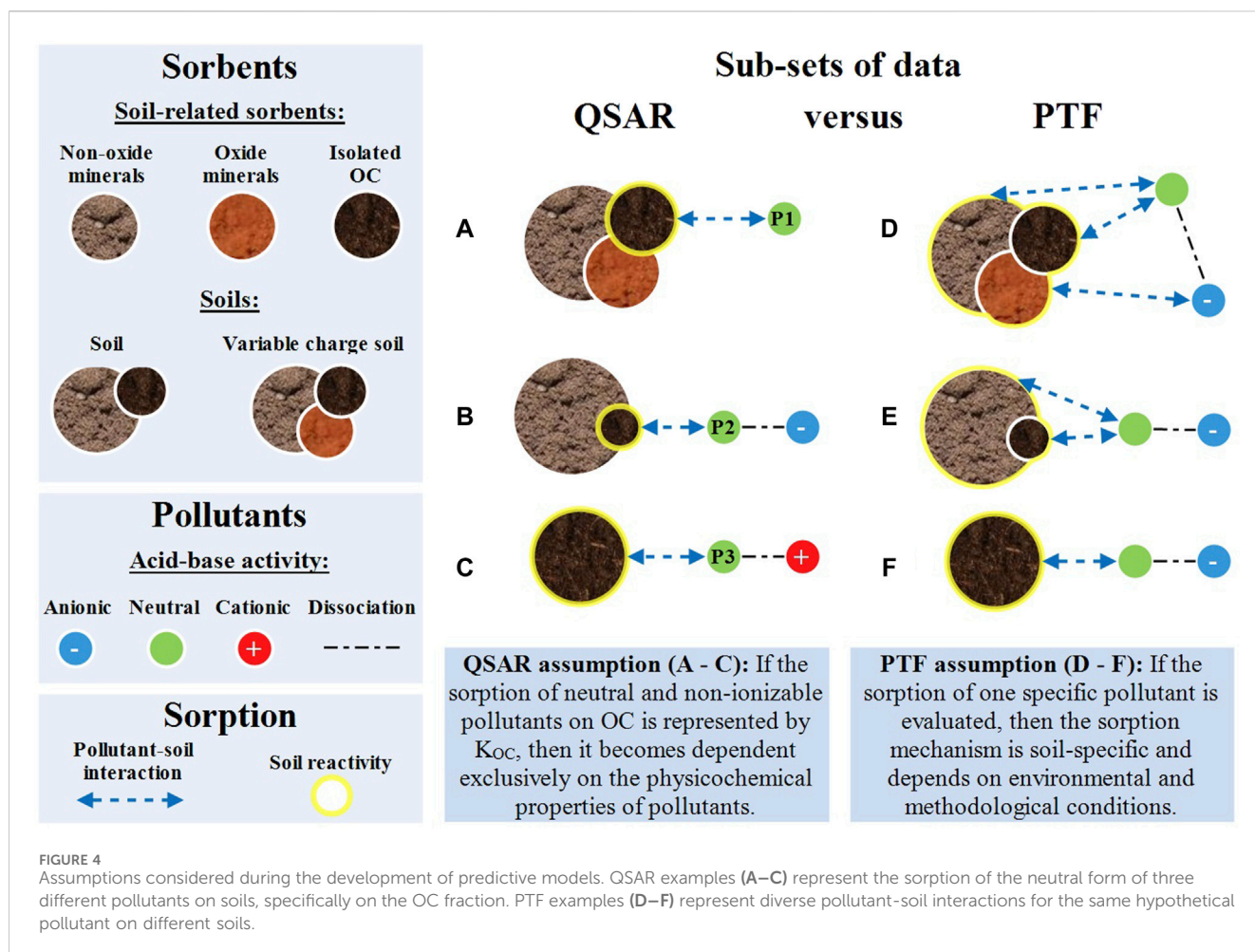### 3.1.2 Data collection and treatment
3.1.2.1 QSAR models

Physicochemical information of sorbents was typically not included in QSAR studies (Wang et al., 2015; Aranda et al., 2016; Rybacka and Andersson, 2016; Berthod et al., 2017; Daré et al., 2017; Olguin et al., 2017; Sabour and Moftakhari Anasori Movahed, 2017; Zhu et al., 2017; Zhang et al., 2018; Cai et al., 2019; Olguin et al., 2019; Kobayashi et al., 2020; Kobayashi and Yoshida, 2021; Muhire et al., 2021; Pandey and Roy, 2021; Cantwell et al., 2022; Jiang et al., 2022). Additionally, methodological conditions used to obtain the experimental sorption coefficient values were neglected during the development of the datasets. Moreover, some sorption coefficients were theoretically derived from other predictive models using the octanol/water partition coefficient (K_{OW}) (Wang et al., 2015; Daré et al., 2017; Sabour and Moftakhari Anasori Movahed, 2017; Muhire et al., 2021; Cantwell et al., 2022; Jiang et al., 2022). Of course, these theoretical data lack a specific experimental methodology and soil/environmental properties that explain their values and guide their interpretation.

The previous findings impact the applicability of QSAR models in two ways: (i) empirical values were used together, independent of their quantification method (e.g., one-point vs. isotherm, batch vs. field-based) or sorption trend (e.g., sorption isotherm linearity); and (ii) datasets in the considered literature were built using mean or median sorption coefficient values such that the amount of data is equivalent to the number of pollutants and soil variability was part of the experimental error. Both issues increase the uncertainty when trying to assess the representational value of data for reliable predictions.

Furthermore, findings impact the reproducibility of QSAR models: (i) only three QSAR models provided the units of sorption coefficients (Wang et al., 2015; Rybacka and Andersson, 2016; Berthod et al., 2017), necessary to evaluate the comparability among empirical values obtained from different studies due to possible changes in the isotherm shape (linearity, 1/n); and (ii) more recent QSAR studies used data from previous articles that were in turn obtained from even older papers, based on well-known databases and the ability to contrast algorithms among QSAR models if they share the same dataset. As a result, several QSAR articles shared their datasets (Olguin et al., 2017; Olguin et al., 2019; Kobayashi and Yoshida, 2021; Daré et al., 2017; Muhire et al., 2021; Wang et al., 2015; Sabour and Moftakhari Anasori Movahed, 2017) or part of the data (Zhang et al., 2018; Pandey and Roy, 2021; Wang et al., 2015; Aranda et al., 2016; Kobayashi et al., 2020). However, we were unable to determine the empirical origin of data used in those articles. Moreover, the amount of data among QSAR articles sharing datasets differed without an explanation, which affects their interpretation and usability.

3.1.2.2 PTF models

In contrast to QSAR, articles concerning PTF included the description of the site and procedure for soil sampling, with most

FIGURE 4
Assumptions considered during the development of predictive models. QSAR examples **(A–C)** represent the sorption of the neutral form of three different pollutants on soils, specifically on the OC fraction. PTF examples **(D–F)** represent diverse pollutant-soil interactions for the same hypothetical pollutant on different soils.

of the sorbents being agricultural soils. Generally speaking, soil samples were superficial, from 0 to 5 (De Gerónimo et al., 2018), 20 (Conde-Cid et al., 2019; Conde-Cid et al., 2020) or 25 cm depth (Kodešová et al., 2015; Klement et al., 2018), with few cases addressing the spatial variability (Kodešová et al., 2015; Singh et al., 2016). In some cases, confounding variables were minimized using soils without application of the pollutants or fertilizers in previous years (De Gerónimo et al., 2018) or by evaluating the presence of pollutants before the sorption study (Conde-Cid et al., 2020).

Additionally, methodological and environmental conditions such as soil:solution ratio, interval of concentrations, background electrolyte, temperature, and contact and equilibrium time impacted the magnitude and interpretation of sorption coefficients and therefore were included during the data collection and treatment. For instance, the selection of the interval of concentrations or the soil:solution ratio impacted the isotherm shape (Dollinger et al., 2015), with several nonlinear sorption isotherms fitting to the Freundlich model (Dollinger et al., 2015; Kodešová et al., 2015; Sidoli et al., 2016; De Gerónimo et al., 2018; Klement et al., 2018; Conde-Cid et al., 2019; Conde-Cid et al., 2020; Hu et al., 2022), including the prediction of the linearity coefficient (1/n) in addition to the sorption coefficient (Dollinger et al., 2015).

All sorption coefficients used in PTF models were quantified experimentally. Most of the PTF studies produced their own data using the same methodological conditions (Kodešová et al., 2015; Sidoli et al., 2016; Singh et al., 2016; De Gerónimo et al., 2018; Klement et al., 2018; Conde-Cid et al., 2019; Conde-Cid et al., 2020). Only in two cases data were collected from other studies (Dollinger et al., 2015; Hu et al., 2022), where methodological differences among studies were included as predictor variables and analyzed during the mechanistic interpretation of predictive models. Additionally, data treatment included a homogenization step when (i) sorption was approximately linear, so K_F and K_d were used jointly (Dollinger et al., 2015; Conde-Cid et al., 2019) or (ii) isotherm linearity was highly variable, affecting the comparability and interpretation of K_F values, where average linearity coefficients (1/n) were calculated for each pollutant and their K_F values were recalculated (Kodešová et al., 2015; Sidoli et al., 2016; Klement et al., 2018).

Another homogenization technique involved the simplification of the sorption mechanisms by minimizing the variability (i) between pollutants, e.g., using pH-dependent pollutants at similar pH values among soils (Conde-Cid et al., 2019) or avoiding mixtures between ionic and non-ionic forms (Sidoli et al., 2016); or (ii) between sorbents, e.g., using unmodified soils or sediments with OC < 20% and comparable background electrolytes (Dollinger et al., 2015).

3.1.2.3 Key insights

QSAR models were focused on a common sorption mechanism applicable through several soils, while PTF models considered local

variability and specific sorption mechanisms, in accordance with our proposed assumptions (Figure 4). This affected the data collection and treatment. For QSAR models, data lack methodological and environmental context because they are assumed as independent of soils (e.g., methodological conditions such as soil:solution ratio could be perceived as soil variability and therefore irrelevant). On the other hand, PTF models implemented a highly detailed procedure, including (i) description of soils, (ii) impacts of methodological and environmental conditions, and (iii) classification and treatment of data in agreement with the previous steps.

3.1.3 Predictor variables
3.1.3.1 QSAR models

Only molecular properties were used by QSAR models to predict sorption coefficients. Those predictor variables, called "descriptors" in QSAR models, were generally related to hydrophobicity, such as K_{OW} (Cai et al., 2019; Muhire et al., 2021) or the number of C-F bonds in a molecule (Jiang et al., 2022). In general, the simplified molecular input line entry system (SMILES), international chemical identifier (InChIKey) and structural data file (SDF) were sufficient to represent the 2D and 3D molecules. Then, a molecular structure optimization method was applied (Wang et al., 2015; Zhu et al., 2017; Zhang et al., 2018; Cai et al., 2019; Jiang et al., 2022). Finally, descriptors were quantified implementing several software solutions such as Dragon (Wang et al., 2015; Sabour and Moftakhari Anasori Movahed, 2017), EPI Suite (Aranda et al., 2016; Olguin et al., 2017), MOLE db (Sabour and Moftakhari Anasori Movahed, 2017), MOE (Berthod et al., 2017), Mordred (Kobayashi et al., 2020; Kobayashi and Yoshida, 2021), Multiwfn (Jiang et al., 2022), Open Babel (Kobayashi et al., 2020), OPERA (Kobayashi and Yoshida, 2021), and PaDEL-Descriptor (Aranda et al., 2016; Pandey and Roy, 2021). These software offer thousands of constitutional, topological, geometrical, electronic, thermodynamic, quantum chemical, and other kinds of theoretical and semi-theoretical descriptors. Descriptors quantified by each software were complementary yet also overlapped, making it necessary to eliminate constant or correlated descriptors in a future step.

Despite the previously described procedure, (i) hydrophobicity was in some cases inadequate for representing the sorption of ionic species, affecting the statistical quality of QSAR models (Rybacka and Andersson, 2016; Berthod et al., 2017), and (ii) the use of molecular descriptors (hydrophobic, hydrogen-bonding and charge-related interactions) to address soil variability produced poor predictive ability (Berthod et al., 2017). Both cases support our proposed assumption (Figure 4) as a requisite to apply QSAR models.

3.1.3.2 PTF models

Physicochemical properties of soils were used as predictor variables for PTF models, including environmental and methodological conditions that varied within the dataset. The most common properties were pH in different solutions, OC, soil texture, and cation exchange capacity (CEC). More properties were added to represent specific soil orders or land uses, such as variable charge (e.g., exchangeable aluminum, crystallized and amorphous oxy-hydroxides) (Sidoli et al., 2016; De Gerónimo et al., 2018; Conde-Cid et al., 2019), salinity (e.g., CaCO$_3$ content, hydrolytic

and exchangeable acidity, base cation saturation) (Kodešová et al., 2015; Klement et al., 2018), or agricultural context (e.g., total organic N content, available P) (Sidoli et al., 2016; Conde-Cid et al., 2019). Some properties showed statistically significant correlations, such as OC with CEC and clay content with iron and aluminum oxides (De Gerónimo et al., 2018). Since these correlations depend on soils they cannot be generalized. Additionally, the quantification method varied among articles. In these cases, different methodological conditions within a dataset were (i) tested as descriptors, e.g., soil:solution ratio and maximum initial concentration of pollutants (Dollinger et al., 2015; Hu et al., 2022) or (ii) used as part of the data splitting (Dollinger et al., 2015).

3.1.3.3 Key insights

According to our proposed assumptions (Figure 4), if the sorption mechanism is independent of soils, then it is not necessary to contextualize predictor variables or include soil descriptors. This explains why QSAR models generally follow an *a posteriori* approach, where a massive pool of molecular descriptors is used, and the mechanistic explanation is derived from the algorithmically selected descriptors to represent the outcome. On the other hand, PTF models explicitly address the complexity of the sorption process, following an *a priori* approach, where they explain the conceptual background of the sorption process and consequently propose a few predictor variables to develop predictive models.

3.1.4 Model equation
3.1.4.1 QSAR models

Databases were split into a training and a test set, used to develop the QSAR model and assess its predictive performance, respectively. In this sense, data splitting helped to evaluate the reliability of QSAR models when applied to external data, providing an estimate of the performance for new pollutants. Ideally, data are uniformly distributed between training and test set. In the literature, the process was random (Wang et al., 2015; Berthod et al., 2017; Sabour and Moftakhari Anasori Movahed, 2017; Muhire et al., 2021; Cantwell et al., 2022; Jiang et al., 2022) or rational, depending on the splitting algorithm, where Y-ranking is the most frequent approach (Zhu et al., 2017; Cai et al., 2019; Olguin et al., 2019; Kobayashi and Yoshida, 2021). Considered training:test set ratios include 14:86 (Aranda et al., 2016), 66:33 (Olguin et al., 2017; Olguin et al., 2019; Kobayashi and Yoshida, 2021; Cantwell et al., 2022), 70:30 (Sabour and Moftakhari Anasori Movahed, 2017), 75:25 (Wang et al., 2015; Daré et al., 2017; Muhire et al., 2021; Pandey and Roy, 2021), 80:20 (Berthod et al., 2017; Zhu et al., 2017; Cai et al., 2019; Pandey and Roy, 2021; Jiang et al., 2022), and 88:12 (Kobayashi et al., 2020). In one case, the effect of dataset size was also evaluated, showing that the division of the training set (N = 643) into eight subsets (N = 79 - 81) produced equivalent QSAR models to those for the whole dataset (Olguin et al., 2019).

Some articles applied mechanistic criteria for splitting, such as the development of different QSAR models based on the whole dataset and specific chemical classes (aliphatic groups, monoaromatic hydrocarbons, diphenyl ethers, polyaromatic hydrocarbons and plant protection products), with their respective training and test sets (Pandey and Roy, 2021), the use of different test sets based on intervals of low, medium and high sorption coefficient values (Daré et al., 2017), the use of several

training and test sets to evaluate the stability of the mathematical equation and its predictability (Berthod et al., 2017), and the development of QSAR models based on the charge of the pollutants (neutral, positively, and negatively charged) (Rybacka and Andersson, 2016; Berthod et al., 2017).

Different algorithms were used to develop the QSAR models, most of them assuming a linear relationship between descriptors and outcome, such as multiple linear regression (MLR) (Wang et al., 2015; Aranda et al., 2016; Berthod et al., 2017; Kobayashi et al., 2020; Kobayashi and Yoshida, 2021; Pandey and Roy, 2021; Jiang et al., 2022), partial least squares regression (PLSR) (Rybacka and Andersson, 2016; Berthod et al., 2017; Daré et al., 2017; Zhu et al., 2017; Cai et al., 2019; Pandey and Roy, 2021), support vector machines (SVM) (Kobayashi et al., 2020; Kobayashi and Yoshida, 2021), and univariate linear regression (ULR) (Berthod et al., 2017; Olguin et al., 2017; Zhang et al., 2018; Olguin et al., 2019). Nonlinear models included gradient boosting decision tree (Kobayashi et al., 2020; Kobayashi and Yoshida, 2021) and neural network-based models (Berthod et al., 2017; Sabour and Moftakhari Anasori Movahed, 2017) algorithms.

MLR was the most frequently used algorithm due to the simple mechanistic explanation derived from those QSAR models. However, previous treatments were required due to the large number of descriptors, e.g., stepwise selection (Wang et al., 2015; Berthod et al., 2017; Pandey and Roy, 2021; Jiang et al., 2022), best subset selection (Pandey and Roy, 2021) and replacement method (Aranda et al., 2016). Additionally, PLSR was useful for dimensionality reduction and to avoid multicollinearity (Zhu et al., 2017; Cai et al., 2019; Pandey and Roy, 2021). On the other hand, nonlinear regressions were able to represent complex relationships between sorption coefficients and descriptors. Finally, ULR was used to assess simple relationships between sorption coefficients and hydrophobicity.

3.1.4.2 PTF models

Data splitting was always related to mechanistic issues, such as the use of different outcomes (Hu et al., 2022), the use of one pollutant per model (Kodešová et al., 2015; Sidoli et al., 2016; Singh et al., 2016; Klement et al., 2018; Conde-Cid et al., 2020) and/or per site or plot from which the data were obtained (Singh et al., 2016), and the methodological conditions and available information about specific physicochemical properties (Dollinger et al., 2015). However, only three articles included training and test sets (Singh et al., 2016; Conde-Cid et al., 2019; Hu et al., 2022), negatively affecting the validation of most of the PTF models.

Algorithms for developing PTF models included MLR (Dollinger et al., 2015; Kodešová et al., 2015; Sidoli et al., 2016; De Gerónimo et al., 2018; Klement et al., 2018; Conde-Cid et al., 2019; Conde-Cid et al., 2020; Hu et al., 2022) with stepwise selection (Dollinger et al., 2015; Sidoli et al., 2016; De Gerónimo et al., 2018), PLSR (Singh et al., 2016) and nonlinear algorithms (Sidoli et al., 2016). One study used principal component analysis (PCA) to guide the interpretation of descriptors for the MLR (De Gerónimo et al., 2018). Some MLR algorithms included the transformation of physicochemical soil properties that did not follow a normal distribution (Conde-Cid et al., 2020), or the use of exponential relationships between sorption coefficients and predictor variables to improve the

statistical quality (from $R^2 < 0.75$ to > 0.92) but changing the mechanistic interpretation (Sidoli et al., 2016).

3.1.4.3 Key insights

Data splitting preceded the generation of a mathematical equation. This had a statistical explanation in QSAR models (i.e., reliability by using training and test sets), with a few articles including characteristics of pollutants. The procedure and the use of several explicit algorithms for developing the QSAR models agrees with the OECD principle P2 (Figure 3). Inversely, PTF models lacked a statistically validated procedure but evaluated diversity and complexity of data and used the data splitting to better represent sorption mechanism, according to pollutant-soil interactions. This procedure is not included in QSAR models because the sorption mechanism was assumed as generalizable and independent of soils (Figure 4).

3.1.5 Model validation
3.1.5.1 QSAR models

The validation of QSAR models was based on the OECD principle P4 (Wang et al., 2015; Sabour and Moftakhari Anasori Movahed, 2017; Kobayashi et al., 2020; Kobayashi and Yoshida, 2021), considering several statistical parameters and procedures classified in two steps: internal validation (training set) related to the goodness-of-fit and robustness, and external validation (test set) to evaluate the predictive performance.

Common statistical parameters for goodness-of-fit included R^2 (Berthod et al., 2017; Daré et al., 2017; Olguin et al., 2017; Sabour and Moftakhari Anasori Movahed, 2017; Zhu et al., 2017; Zhang et al., 2018; Cai et al., 2019; Olguin et al., 2019; Kobayashi et al., 2020; Kobayashi and Yoshida, 2021; Muhire et al., 2021; Pandey and Roy, 2021; Cantwell et al., 2022) and adjusted R^2 (Wang et al., 2015; Muhire et al., 2021; Jiang et al., 2022), F-Test value (Zhang et al., 2018; Muhire et al., 2021; Cantwell et al., 2022), standard error of the estimate (Zhu et al., 2017; Zhang et al., 2018; Cai et al., 2019; Kobayashi et al., 2020; Cantwell et al., 2022), residual sum of squares (Olguin et al., 2017; Kobayashi et al., 2020), root mean square error (RMSE) (Wang et al., 2015; Daré et al., 2017; Olguin et al., 2017; Sabour and Moftakhari Anasori Movahed, 2017; Olguin et al., 2019; Kobayashi and Yoshida, 2021; Muhire et al., 2021; Jiang et al., 2022), *p*-value of descriptors contained in the QSAR model (Zhu et al., 2017; Cai et al., 2019; Muhire et al., 2021; Jiang et al., 2022), variance inflation coefficient to evaluate multicollinearity (Jiang et al., 2022), mean absolute error (Pandey and Roy, 2021), and concordance correlation coefficient (CCC) (Olguin et al., 2017; Sabour and Moftakhari Anasori Movahed, 2017; Olguin et al., 2019; Kobayashi and Yoshida, 2021).

Robustness was typically addressed through one of the following procedures: "leave-one-out" cross-validation (Wang et al., 2015; Aranda et al., 2016; Berthod et al., 2017; Daré et al., 2017; Olguin et al., 2017; Sabour and Moftakhari Anasori Movahed, 2017; Zhang et al., 2018; Cai et al., 2019; Olguin et al., 2019; Kobayashi et al., 2020; Kobayashi and Yoshida, 2021; Muhire et al., 2021; Pandey and Roy, 2021; Cantwell et al., 2022; Jiang et al., 2022), "leave-many-out" cross-validation (Olguin et al., 2017; Olguin et al., 2019), and bootstrapping (Wang et al., 2015). Additionally, Y-scrambling was used to detect or discard chance correlations (Aranda et al., 2016; Daré et al., 2017; Olguin et al., 2017; Sabour and Moftakhari

Anasori Movahed, 2017; Zhang et al., 2018; Olguin et al., 2019; Kobayashi and Yoshida, 2021; Muhire et al., 2021; Pandey and Roy, 2021). Other statistical parameters such as RMSE and CCC for the internal validation were also used (Daré et al., 2017; Olguin et al., 2017; Zhang et al., 2018; Olguin et al., 2019; Kobayashi and Yoshida, 2021; Muhire et al., 2021).

External validation was evaluated through different indicators, such as variance explained in external prediction (Wang et al., 2015; Daré et al., 2017; Olguin et al., 2017; Sabour and Moftakhari Anasori Movahed, 2017; Zhu et al., 2017; Zhang et al., 2018; Cai et al., 2019; Olguin et al., 2019; Kobayashi and Yoshida, 2021; Muhire et al., 2021; Pandey and Roy, 2021; Cantwell et al., 2022; Jiang et al., 2022), modified coefficient of determination of the external validation (Daré et al., 2017; Olguin et al., 2017; Sabour and Moftakhari Anasori Movahed, 2017; Zhang et al., 2018; Olguin et al., 2019; Kobayashi et al., 2020; Muhire et al., 2021; Pandey and Roy, 2021), standard error of prediction (Zhu et al., 2017; Cai et al., 2019; Cantwell et al., 2022), RMSE of validation (Wang et al., 2015; Sabour and Moftakhari Anasori Movahed, 2017; Zhang et al., 2018; Olguin et al., 2019; Kobayashi and Yoshida, 2021; Muhire et al., 2021), external CCC (Zhang et al., 2018; Olguin et al., 2019; Kobayashi and Yoshida, 2021), and mean absolute error (Pandey and Roy, 2021).

3.1.5.2 PTF models

Validation of PTF models was scarce and focused on goodness-of-fit, using R^2 or adjusted R^2 (Kodešová et al., 2015; Sidoli et al., 2016; Singh et al., 2016; Klement et al., 2018; Conde-Cid et al., 2019; Conde-Cid et al., 2020), p-value (Kodešová et al., 2015; Klement et al., 2018; Conde-Cid et al., 2019) and standard error (Singh et al., 2016), but not including an analysis of overfitting (e.g., observation: descriptor ratio). Two articles assessed the model robustness through cross-validation (Dollinger et al., 2015) and bootstrap methods (De Gerónimo et al., 2018). Articles that considered validation sets followed different approaches to validate their models: (i) developing the PTF model using the training set but quantifying R^2, Nash-Sutcliffe efficiency, RMSE, and absolute error only for the validation set (Hu et al., 2022), thereby causing the model to lack goodness-of-fit and robustness, (ii) plotting the measured vs. estimated sorption coefficient values for the training and test set and checking how many data fell within the interval of the measured value ± 2 units (Conde-Cid et al., 2019), or (iii) applying the same goodness-of-fit parameters for the validation set (R^2, standard error) (Singh et al., 2016).

3.1.5.3 Key insights. QSAR models present a higher statistical quality than PFT models, due to the application of training and test sets, the high number of statistical parameters applied to the data, and their consistency among different studies. This is not related to our proposed assumptions (Figure 4) but the institutionalization of QSAR models with respect to PTFs (P2 and P4, Figure 3).

3.1.6 Applicability of predictive models
3.1.6.1 QSAR models

The applicability domain (AD) is a theoretical chemical space where QSAR models make reliable predictions (Kobayashi et al., 2020; Kobayashi and Yoshida, 2021). This region is defined by the diversity of pollutants (molecular structures) in the training set and the descriptors that are used to predict their endpoints (Aranda

et al., 2016; Zhu et al., 2017). The AD is specific to each QSAR model, and reliability is only possible to assess for molecules and properties that fall within this chemical space, based on similarity (Daré et al., 2017; Zhu et al., 2017). Otherwise, a prediction is an unreliable model extrapolation (Aranda et al., 2016; Zhu et al., 2017). Without an explicit definition of the AD, a predictive model does not meet the OECD principle P3 (Zhang et al., 2018).

AD was quantified by standardization (Wang et al., 2015; Daré et al., 2017; Sabour and Moftakhari Anasori Movahed, 2017; Zhu et al., 2017; Zhang et al., 2018; Cai et al., 2019; Olguin et al., 2019; Kobayashi et al., 2020; Kobayashi and Yoshida, 2021; Pandey and Roy, 2021), leverage (Wang et al., 2015; Aranda et al., 2016; Daré et al., 2017; Sabour and Moftakhari Anasori Movahed, 2017; Zhu et al., 2017; Zhang et al., 2018; Cai et al., 2019; Olguin et al., 2019; Muhire et al., 2021), Euclidean distance (Kobayashi et al., 2020; Kobayashi and Yoshida, 2021), and one-class support vector machines (Kobayashi and Yoshida, 2021). These methods were applied to detect outliers (usually defined as > 3.0σ from the mean) and/or influential points (leverage > threshold). AD was commonly visualized through a Williams plot considering the standardized cross-validated residuals *versus* leverage values of pollutants (Wang et al., 2015; Sabour and Moftakhari Anasori Movahed, 2017; Zhu et al., 2017; Zhang et al., 2018; Cai et al., 2019; Olguin et al., 2019; Muhire et al., 2021; Jiang et al., 2022). Here, outliers and influential points were molecular structures, and their analysis was based on molecular descriptors, delimiting the scope and interpretability of QSAR models (Cai et al., 2019; Jiang et al., 2022).

3.1.6.2 PTF models

The considered PTF models did not include an AD. Therefore, PTF model applicability was not statistically validated.

3.1.6.3 Key insights

QSAR models presented a clearly defined AD, guided by the OECD (P3, Figure 3). AD was independent of methodological or environmental conditions from which the empirical values are obtained, which fits with the QSAR assumption that we proposed (Figure 4) and impacts the OECD principle P5 (Figure 3). On the other hand, PTF models lack a defined AD but used soil physicochemical properties and methodological conditions as predictor variables, implying that their AD would be defined by the diversity of pollutant-soil interactions, whose interpretability depends on soils and local conditions.

3.1.7 Regulatory purposes
3.1.7.1 QSAR models

In general, QSAR models were considered as successful for estimating sorption coefficients and were applied to environmental risk assessment (Berthod et al., 2017; Sabour and Moftakhari Anasori Movahed, 2017; Zhang et al., 2018; Cai et al., 2019; Kobayashi et al., 2020; Kobayashi and Yoshida, 2021; Muhire et al., 2021; Jiang et al., 2022), helping the design of new molecules with less environmental impact (Sabour and Moftakhari Anasori Movahed, 2017; Kobayashi et al., 2020; Muhire et al., 2021; Jiang et al., 2022), providing objective decisions (Kobayashi et al., 2020; Kobayashi and Yoshida, 2021) and assessing soil remediation and potential leaching (Sabour and Moftakhari Anasori Movahed, 2017).

TABLE 2 Summary of the information extracted from the experimental articles from the literature (presented in the same order as in Supplementary Table S4).

		Sources of variability[a]		Characterization of pesticides					Trends found in the study	
#	Ref.	Soil (SV)	Other (OV)	Pesticides studied[b]	Target[c]	Acid-base activity[d]	Chemical class[e]	Chemical form in the study	Method to analyze trends[f]	Variables affecting sorption[g]
1	Kaur et al. (2022)	Soil	None	P30	Herb	(V)WA	G1	Anionic	Unclear	OC and clay content
2	Pavão et al. (2022)	Soil	None	P34	Herb	(V)WA	G2	pH-dependent	PCA	PCA1 (clay, base saturation, CEC), PCA2 (total OC and pH)
3	Siek et al. (2021)	Soil, Spatial	None	P36	Fung	O_{AB}	G1	pH-dependent	Correlation matrix, PLS	Specific types of OC and acidity
4	Cáceres-Jensen et al. (2021)	Soil	None	P1	Herb	(V)SA	G4	Mostly anionic	Correlation matrix, MLR	IEP of mineral oxides in variable-charged soils where IEP > pH
5	Meftaul et al. (2021)	Soil	None	P17	Herb	(V)SA	G3	pH-dependent	Correlation matrix, PCA	K_d^{op} vs. $OC^{(+)}$, Fe/Al oxides$^{(+)}$, clay$^{(+)}$, silt$^{(+)}$, pH$^{(-)}$ and sand$^{(-)}$
6	Chen et al. (2021)	Soil	None	P32	Herb	Non-I	G1	Not applicable	Correlation	K_F vs. $CEC^{(+)}$ and $\%clay^{(+)}$
7	Beringer et al. (2021)	Soil	None	P8	Insec	SB	G1	Not mentioned	Not applicable	Not applicable
8	Xu et al. (2020)	Treat	None	P37	Insec	Non-I	G1	Not applicable	Not applicable	Not considered
9	Zhao et al. (2020)	Soil	None	P3	Herb	(V)WB	G1	Neutral	Comparison of data	Structural differences of sorbents
10	Meftaul et al. (2020)	Soil	None	P1	Herb	(V)SA	G4	Anionic	Comparison of data	OC content, clay content, Al/Fe oxides, and soil acidity
11	García-Delgado et al. (2020)	Soil, Treat	Pollut	P5, P15, P33, P38	Herb	(V)WA, Non-I	G2	Not mentioned	Comparison of data, MLR, PCA	OC content, polarity of sorbent, and pesticide properties (K_{OW})
12	das Chagas et al. (2020)	Soil, Treat	None	P14	Herb	Non-I	G2	Not applicable	Comparison of data	Lime addition (associated to the OC content) and the presence of $Ca^{+2}_{(aq)}$ and $Mg^{+2}_{(aq)}$
13	Wang et al. (2020)	None	Pollut	P4, P10, P11, P12, P21	Insec, Fung	(V)SA, Non-I, (V)WB, O_{AB}	G1, G2, G3	pH-dependent	Correlation	K_F vs. K_{OW}

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TABLE 2 (*Continued*) Summary of the information extracted from the experimental articles from the literature (presented in the same order as in Supplementary Table S4).

		Sources of variability[a]		Characterization of pesticides					Trends found in the study	
#	Ref.	Soil (SV)	Other (OV)	Pesticides studied[b]	Target[c]	Acid-base activity[d]	Chemical class[e]	Chemical form in the study	Method to analyze trends[f]	Variables affecting sorption[g]
14	Caceres-Jensen et al. (2020)	Soil	None	P27	Herb	(V)WA	G2	pH-dependent	Comparison of data, PCA, cluster analysis	OC and acidity (hydrophobic interactions); CEC and mineral surface area (other interactions)
15	Agbaogun and Fischer (2020)	Soil	Pollut	P5, P14, P19, P20, P26	Herb	Non-I, O_{AB}	G2	Not considered	Comparison of data, correlation matrix	K_F vs. pH, Fe oxides, OC, among others (depending on the pesticide). Average value of K_F vs. molecular properties (log K_{OW} and M_W)
16	Caceres-Jensen et al. (2019)	Soil	None	P17	Herb	(V)SA	G3	Ionizable	Comparison of data	OC, pH and IEP
17	Dos Santos et al. (2019)	Soil, Treat	None	P18	Herb	(V)WB	G1	pH-dependent	Comparison of data	Lime addition (associated to the OC content and changes in pH)
18	Pereira et al. (2019)	Soil	None	P17	Herb	(V)SA	G3	Ionizable	Comparison of data	OC and Fe/Al oxides
19	Loffredo et al. (2019)	Soil	None	P25	Herb	(V)SA	G1	Not mentioned	Comparison of data, correlation	K_d vs. OC$^{(+)}$, ash content$^{(-)}$, moisture$^{(-)}$ and EC$^{(-)}$
20	Góngora-Echeverría et al. (2019)	None	Pollut	P1, P3, P9, P17	Herb, Insec	(V)SA, (V)WB	G1, G3, G4	Not mentioned	Not applicable	Not applicable
21	Ben Salem et al. (2019)	None	Pollut	P6, P13	Insec	Non-I	G3	Not applicable	Not applicable	Not applicable
22	Silva et al. (2018)	Treat	None	P7	Herb	Non-I	G1	Not applicable	Comparison of data, correlations	K_F vs. % biochar/d_P
23	Pose-Juan et al. (2018)	Treat	Pollut	P23, P31, P38	Herb	(V)WA, Non-I	G2, G4	Two ionizable, one neutral	Comparison of data, correlations	K_d^{op} vs. DOC (for P23) or pH (for P38)
24	Khorram et al. (2018)	Treat	None	P16	Herb	(V)SA	G3	Anionic	Comparison of data	K_F vs. % biochar$^{(+)}$, specific surface area$^{(+)}$ and DOC$^{(-)}$
25	Paradelo et al. (2018)	Soil	None	P22	Herb	(V)WA	G4	Ionizable and neutral forms	Comparison of data	OC content
26	Skeff et al. (2018)	Soil	None	P17	Herb	(V)SA	G3	Ionizable	Comparison of data	K_F vs. Fe/Al content$^{(+)}$, pH

(Continued on following page)

TABLE 2 (*Continued*) Summary of the information extracted from the experimental articles from the literature (presented in the same order as in Supplementary Table S4).

		Sources of variability[a]		Characterization of pesticides					Trends found in the study	
#	Ref.	Soil (SV)	Other (OV)	Pesticides studied[b]	Target[c]	Acid-base activity[d]	Chemical class[e]	Chemical form in the study	Method to analyze trends[f]	Variables affecting sorption[g]
27	Sousa et al. (2018)	Soil, Treat	Pollut, Exp	P14, P18	Herb	Non-I, (V)WB	G1, G2	Neutral	Comparison of data	OC, CEC, interaction between pesticides (mixture)
28	Kaur et al. (2018)	Soil	Exp	P29	Herb	(V)SA	G4	Not considered	Comparison of data	Minerals (size and composition) and temperature
29	Mosquera-Vivas et al. (2018)	Soil, Spatial	None	P36	Fung	O_{AB}	G1	Protonated and neutral forms	Comparison of data, correlation	K_F vs. $OC^{(+)}$
30	Marín-Benito et al. (2017)	Soil, Treat	Pollut	P2, P20, P24	Herb, Fung	(V)SA, Non-I	G2	Not considered	Comparison of data	For K_F: pesticides, minerals (size and composition), OC (except alachlor). For K_d^{op}: OC content added by amendments
31	Alfonso et al. (2017)	Soil	Pollut	P9, P13, P28, P35	Insec	(V)SA, Non-I, O_{AB}	G3	Not mentioned	Comparison of data, ANOVA	For K_F: Water solubility of pesticides (not all the cases)

[a]Sources of variability are described in methodology, Section 2.4.

[b]Pesticides are described in Table 3.

[c]**Fung:** fungicide, **Herb:** herbicide, **Insec:** insecticide.

[d]**(V)SA:** strong or very strong acid, **(V)WA:** weak or very weak acid, **(V)WB:** weak or very weak base, **Non-I:** non-ionizable, **SB:** strong base.

[e]**G1:** heterocyclic compound, **G2:** amide derivative, **G3:** Cl- and PO_3-derivatives, **G4:** other chemical class.

[f]**ANOVA:** analysis of variance, **MLR:** multiple linear regression, **PCA:** principal component analysis, **PLS:** partial least squares.

[g]We included the superscript "op" for outcomes that were quantified from one specific initial concentration of pollutant (one-point K_d or K_{OC}) instead of a sorption isotherm. Additionally, the superscripts "(+)" and "(−)" represent positive and negative correlations, respectively. **CEC:** cation exchange capacity, **DOC:** dissolved organic carbon, **d_p:** diameter of particles assuming they are spherical, **EC:** electrical conductivity, **IEP:** isoelectric point, **K_{OW}:** octanol/water partition coefficient, **M_W:** molecular weight, **OC:** organic carbon.

3.1.7.2 PTF models

PTF models were also considered successful and useable for environmental fate and risk assessment (Dollinger et al., 2015; Kodešová et al., 2015; Singh et al., 2016; Hu et al., 2022), and identification of vulnerable soils (Conde-Cid et al., 2020; Hu et al., 2022), helping the developing of mitigation strategies and management practices when necessary (Conde-Cid et al., 2020; Hu et al., 2022). However, the use of PTF models was generally suggested more cautiously than for QSARs. For instance, PTF models were proposed as screening methods for regional approaches if local soils were included (Singh et al., 2016). So, their validity depends on non-soil variables such as the pollutants and environmental conditions (Hu et al., 2022). Furthermore, their descriptors and the interval of initial concentration for calculating sorption coefficients should be verified with new datasets if used on different soils (Dollinger et al., 2015; Kodešová et al., 2015).

3.1.7.3 Key insights

QSAR models can be used for regulatory purposes for any soil at any condition. However, QSAR reliability is restricted to the validity of their assumption (Figure 4), which in turn depends on the main sorption mechanism within the dataset. On the other hand, PTF models represent diverse sorption mechanisms at local scale. In this sense, QSAR and PTF models are not exclusive but complementary.

3.2 Literature describing empirical findings

Here, we describe the main trends found in empirical studies. We focused the results on pesticides attributes and sources of variability explored within the studies, shown per article and pesticide in Tables 2, 3, respectively. Information in Table 2 shows the sources of variability addressed per article, characterization of pesticides (name of pesticides studied per

TABLE 3 Summary of the information about pesticides extracted from the experimental articles from the literature.

Pesticide		Characterization of pesticides[a]			Studies from literature		Characterization of studies[b]	
ID	Name	Target	Acid-base activity	Chemical class	#	Ref.	Sum of SV	Sum of OV
P1	2,4-D	Herb	(V)SA	G4	3	(Góngora-Echeverría et al., 2019; Meftaul et al., 2020; Cáceres-Jensen et al., 2021)	None, Soil	None, Pollut
P2	Alachlor	Herb	(V)SA	G2	1	Marín-Benito et al. (2017)	Soil, Treat	Pollut
P3	Atrazine	Herb	(V)WB	G1	2	(Góngora-Echeverría et al., 2019; Zhao et al., 2020)	None, Soil	None, Pollut
P4	Carbendazim	Fung	(V)WB	G2	1	Wang et al. (2020)	None	Pollut
P5	Chlorotoluron	Herb	Non-I	G2	2	(Agbaogun and Fischer, 2020; García-Delgado et al., 2020)	Soil, Treat	Pollut
P6	Chlorpyrifos	Insec	Non-I	G3	1	Ben Salem et al. (2019)	None	Pollut
P7	Clomazone	Herb	Non-I	G1	1	Silva et al. (2018)	Treat	None
P8	Clothianidin	Insec	SB	G1	1	Beringer et al. (2021)	Soil	None
P9	Diazinon	Insec	(V)SA	G3	2	(Alfonso et al., 2017; Góngora-Echeverría et al., 2019)	None, Soil	Pollut
P10	Dichlorvos	Insec	Non-I	G3	1	Wang et al. (2020)	None	Pollut
P11	Difenoconazole	Fung	(V)SA	G1	1	Wang et al. (2020)	None	Pollut
P12	Diflubenzuron	Insec	O_{AB}	G2	1	Wang et al. (2020)	None	Pollut
P13	Dimethoate	Insec	Non-I	G3	2	(Alfonso et al., 2017; Ben Salem et al., 2019)	None, Soil	Pollut
P14	Diuron	Herb	Non-I	G2	3	(Agbaogun and Fischer, 2020; Sousa et al., 2018; das Chagas et al., 2020)	Soil, Treat	None, Pollut, Exp
P15	Flufenacet	Herb	Non-I	G2	1	García-Delgado et al. (2020)	Soil, Treat	Pollut
P16	Fomesafen	Herb	(V)SA	G3	1	Khorram et al. (2018)	Treat	None
P17	Glyphosate	Herb	(V)SA	G3	5	(Skeff et al., 2018; Caceres-Jensen et al., 2019; Góngora-Echeverría et al., 2019; Pereira et al., 2019; Meftaul et al., 2021)	None, Soil	None, Pollut
P18	Hexazinone	Herb	(V)WB	G1	2	(Sousa et al., 2018; Dos Santos et al., 2019)	Soil, Treat	None, Pollut, Exp
P19	Isoproturon	Herb	Non-I	G2	1	Agbaogun and Fischer (2020)	Soil	Pollut
P20	Linuron	Herb	Non-I	G2	2	(Marín-Benito et al., 2017; Agbaogun and Fischer, 2020)	Soil, Treat	Pollut
P21	Malathion	Insec	Non-I	G3	1	Wang et al. (2020)	None	Pollut
P22	Mecoprop	Herb	(V)WA	G4	1	Paradelo et al. (2018)	Soil	None
P23	Mesotrione	Herb	(V)WA	G4	1	Pose-Juan et al. (2018)	Treat	None
P24	Metalaxyl	Fung	(V)SA	G2	1	Marín-Benito et al. (2017)	Soil, Treat	Pollut
P25	Metribuzin	Herb	(V)SA	G1	1	Loffredo et al. (2019)	Soil	None
P26	Monuron	Herb	O_{AB}	G2	1	Agbaogun and Fischer (2020)	Soil	Pollut
P27	Nicosulfuron	Herb	(V)WA	G2	1	Caceres-Jensen et al. (2020)	Soil	None
P28	Parathion-methyl	Insec	O_{AB}	G3	1	Alfonso et al. (2017)	Soil	Pollut
P29	Pendimethalin	Herb	(V)SA	G4	1	Kaur et al. (2018)	Soil	Exp
P30	Penoxsulam	Herb	(V)WA	G1	1	Kaur et al. (2022)	Soil	None
P31	Pethoxamid	Herb	Non-I	G2	1	Pose-Juan et al. (2018)	Treat	None
P32	Pinoxaden	Herb	Non-I	G1	1	Chen et al. (2021)	Soil	None

TABLE 3 (*Continued*) Summary of the information about pesticides extracted from the experimental articles from the literature.

Pesticide		Characterization of pesticides[a]			Studies from literature		Characterization of studies[b]	
ID	Name	Target	Acid-base activity	Chemical class	#	Ref.	Sum of SV	Sum of OV
P33	Prosulfocarb	Herb	Non-I	G2	1	García-Delgado et al. (2020)	Soil, Treat	Pollut
P34	Sulfometuron-methyl	Herb	(V)WA	G2	1	Pavão et al. (2022)	Soil	None
P35	Sulfotep	Insec	O_{AB}	G3	1	Alfonso et al. (2017)	Soil	Pollut
P36	Tebuconazole	Fung	O_{AB}	G1	2	(Mosquera-Vivas et al., 2018; Siek et al., 2021)	Soil, Spatial	None
P37	Thiacloprid	Insec	Non-I	G1	1	Xu et al. (2020)	Treat	None
P38	Triasulfuron	Herb	(V)WA	G2	2	(Pose-Juan et al., 2018; García-Delgado et al., 2020)	Soil, Treat	None, Pollut

[a]Abbreviations for targets, acid-base activities and chemical classes are described in Table 2.
[b]Sources of variability are described in methodology, Section 2.4. In this Table, we informed the sum of sources of variability evaluated in all the studies from literature.

article, targets, acid-base activities, chemical classes, and chemical forms in the study), and main trends found in the study. Additionally, the name of the pesticides is shown in Table 3, including their characterization per pesticide, the articles that studied every pesticide and the characterization of those articles (sum of sources of variability addressed per pesticide).

3.2.1 Pesticide attributes
3.2.1.1 *Target*
We identified three pesticide types in the literature: herbicides (N = 24, 63% of studied pesticides), insecticides (N = 10, 26%), and fungicides (N = 4, 11%), which reflects the trend in global usage (De et al., 2014). Among all articles, N = 24 (77%) included herbicides.

3.2.1.2 Acid-base activity
A large percentage of pesticides had no or low pH-dependence: N = 14 (37%) non-ionizable, N = 6 (16%) (very) weak acid, and N = 3 (8%) (very) weak base. Furthermore, acids were more common than bases, with only one article studying a strong base.

3.2.1.3 Chemical class
Heterocyclic compounds and amide derivatives were frequent among pesticides N = 10 (26%) and articles N = 13 (42%).

3.2.1.4 Key insights
A heterogeneous distribution of targets, acid-base activities and chemical classes was found in the literature for articles and pesticides. We related trends to the occurrence of the most frequent pesticides: glyphosate, 2,4-D and diuron (Table 3; Supplementary Figure S2), which are strong acid herbicides and are present in 10 out of 31 articles (32%). These pesticides have been found frequently in water bodies in North America (glyphosate) and Australia (2,4-D and diuron) (Sharma et al., 2019). Furthermore, glyphosate and 2,4-D are commonly used in Argentina, North/Central America, and Africa (Sharma et al., 2019), and studied using PTF models (Dollinger et al., 2015; Sidoli et al., 2016; Singh et al., 2016; De Gerónimo et al., 2018).

3.2.2 Sources of variability
Some of the 31 articles studied one source of variability, while others addressed combinations. Their distribution is shown in Figure 5.

In descending order, we found that articles studied (i) SV [soil] > SV [soil, treat] > SV [treat] > SV [none] > SV [soil, spatial] for soil variability, with seven out of 31 articles studying different sources of soil variability together, and (ii) OV [none] > OV [pollut] > OV [exp] = OV [pollut, exp] for other sources of variability, with only one out of 31 articles studying different sources of variability.

3.2.2.1 Complexity and uncertainty
Sources of variability contrasted in complexity: (i) soil variability involved several sorbents, treatments and/or topographic conditions. Samples had different physicochemical properties, so the interpretation of trends may involve multiple potentially valid explanations, including the presence of confounding variables. Then, these studies are useful to represent real scenarios of environmental concern, but their evaluation of sorption mechanisms is limited due to the inherent uncertainty of the experimental design. On the other hand, (ii) other sources of variability generally involved one sorbent, modifying one specific variable at controlled values (e.g., temperature, pH), giving simpler interpretations that are only locally valid but have potential to be extrapolated in future research.

Three different approaches were used to interpret results, based on their complexity and limitations: (i) conceptual comparisons without statistical tools when only two contrasting cases were studied, e.g., two soils, treatments, or pollutants; (ii) correlations between selected physicochemical properties of sorbents or pollutants (Khorram et al., 2018; Pose-Juan et al., 2018; Silva et al., 2018; Ben Salem et al., 2019; Góngora-Echeverría et al., 2019; Wang et al., 2020; Xu et al., 2020); and (iii) statistical tools applied to all possible variables with the purpose of reducing uncertainty when interpreting experimental studies. Common statistical tools were similar to those used in predictive models: PCA (Caceres-Jensen et al., 2020; García-Delgado et al., 2020; Meftaul et al., 2021; Pavão et al., 2022), regression models (García-Delgado et al., 2020; Cáceres-Jensen et al., 2021; Siek et al., 2021), cluster analysis (Caceres-Jensen
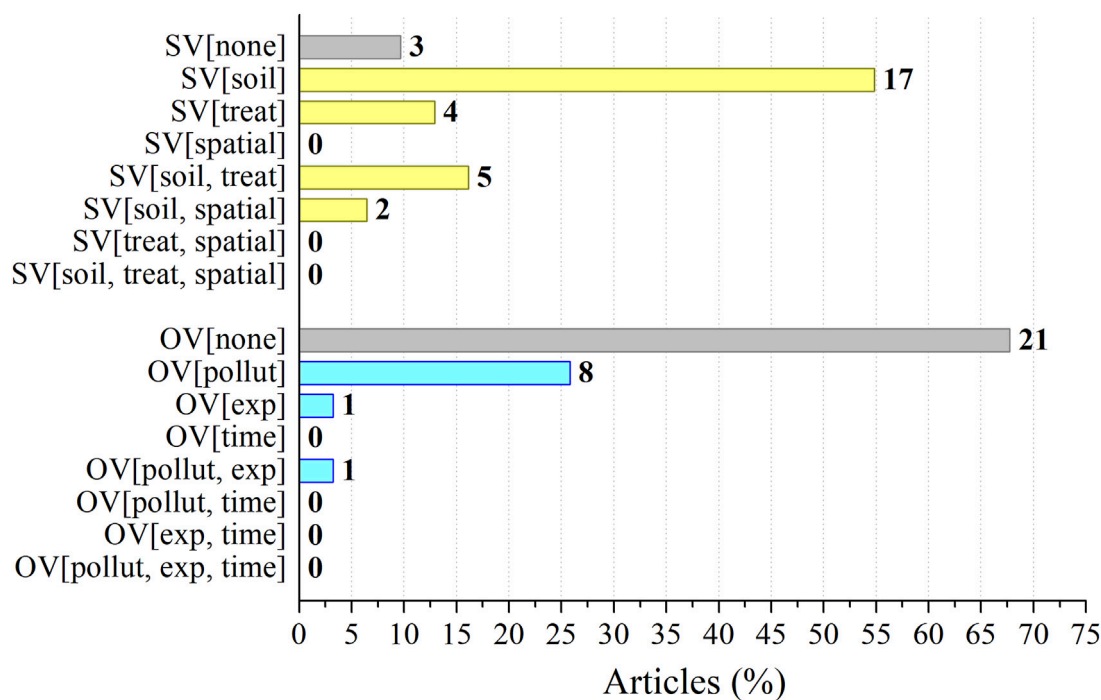
FIGURE 5
Soil variability (SV, yellow) and other sources of variability (OV, light blue) studied in the literature. Gray bars represent a lack of variability (SV [none] and OV [none]). Numbers to the right of each bar represent the number of articles.

et al., 2020), multivariate ANOVA analysis (Alfonso et al., 2017), and correlation matrices between (i) sorption coefficients and physicochemical properties (Mosquera-Vivas et al., 2018; Loffredo et al., 2019; Agbaogun and Fischer, 2020; Cáceres-Jensen et al., 2021; Chen et al., 2021; Siek et al., 2021), (ii) sorption coefficients and pairwise interactions to represent the effect of the interaction between physicochemical properties on sorption (Cáceres-Jensen et al., 2021), and (iii) physicochemical properties to explore multicollinearity and avoid biased interpretations (Agbaogun and Fischer, 2020; Cáceres-Jensen et al., 2021; Siek et al., 2021).

3.2.2.2 Key insights

Soil variability, especially SV [soil], was more frequent in the literature than other sources of variability (Table 2; Figure 5). Additionally, differences in complexity produced different approaches to interpret results, where the use of statistical tools within studies and comparison among studies affect their reliability and extrapolation.

3.3 Evidence-based analysis of the predictive model assumptions

This section explores the QSAR and PTF assumptions from an empirical perspective to simplify their analysis and discussion in Section 4.

3.3.1 Analysis of QSAR assumptions

Sorption coefficients correlated positively with OC content and composition for non-ionizable or neutral pesticides in articles that

investigated SV [soil] (Paradelo et al., 2018; Sousa et al., 2018; Agbaogun and Fischer, 2020; Caceres-Jensen et al., 2020; García-Delgado et al., 2020; Pavão et al., 2022). The same trend was observed for various aromatic pesticides (Mosquera-Vivas et al., 2018; Paradelo et al., 2018; Sousa et al., 2018; Dos Santos et al., 2019; Loffredo et al., 2019; Meftaul et al., 2020; Siek et al., 2021), including a positive correlation between sorption coefficients and exogenous OC such as biochar (Silva et al., 2018). These correlations were associated with hydrophobic and polar sorption mechanisms.

When sorption on OC was exclusively hydrophobic, the previous trend was accompanied for (i) a negative correlation between sorption coefficients and pH for non-ionizable or neutral pesticides (Paradelo et al., 2018; Caceres-Jensen et al., 2020; Pavão et al., 2022), and (ii) a negative or positive correlation between sorption coefficients and solubility or lipophilicity (e.g., K_{OW}), respectively (Silva et al., 2018; Sousa et al., 2018; Agbaogun and Fischer, 2020; García-Delgado et al., 2020; Wang et al., 2020). These trends imply that only the neutral form of pesticides is being sorbed, sorption occurs on OC, and the sorption coefficient depends on pesticides properties (Figures 4A–C).

However, the previous trend is not always valid. For non-ionizable aromatic and heterocyclic compounds, physicochemical properties such as pH (Dos Santos et al., 2019; Siek et al., 2021), CEC (Sousa et al., 2018; Chen et al., 2021), oxide mineral content (Meftaul et al., 2020), size of particles (Silva et al., 2018; Meftaul et al., 2020; Chen et al., 2021), among others (Loffredo et al., 2019; Agbaogun and Fischer, 2020; Chen et al., 2021; das Chagas et al., 2020) were found to be relevant. This was explained by different sorption mechanisms (hydrophobic > polar > others), which may occur together. For example, π-interactions can be hydrophobic (e.g., n-π and π-π stacking of heterocyclic pollutants on aromatic-C from soil OC)

(Agbaogun and Fischer, 2020; García-Delgado et al., 2020; Zhao et al., 2020) or polar (e.g., π-π electron-donor-acceptor) (Zhao et al., 2020), and the affinity difference between aromatic and aliphatic interactions may be relevant (García-Delgado et al., 2020). Additionally, the addition of biochar or the presence of competitive sorption induced changes in the isotherm shape (Silva et al., 2018; Sousa et al., 2018) (i.e., linearity coefficients (1/n) were also needed to describe changes in sorption trends), affecting the outcome selection and interpretation of sorption coefficients.

In addition, we found four scenarios in the literature where K_{OC} did not imply that sorption is independent of soil properties: (i) the presence of non-hydrophobic sorption and the interaction between OC and other soil components may produce correlations between the sorption of neutral pollutants and clay or CEC (Caceres-Jensen et al., 2020; Chen et al., 2021; Pavão et al., 2022), (ii) the hydrophobic sorption may be negatively affected by polar interactions (García-Delgado et al., 2020), (iii) the composition of the soil solution may affect the sorption of non-ionizable pollutants, such as diuron in presence of divalent cations (das Chagas et al., 2020), and (iv) sorption coefficients may correlate with pesticide and soil properties at the same time, e.g., the average sorption of non-ionizable pesticides on soils may depend on K_{OW} but the specific sorption of each pollutant is related to soil properties (Agbaogun and Fischer, 2020).

3.3.1.1 Key insights

The sorption of neutral and non-ionizable pollutants occurs preferably on OC and could be represented by K_{OC}, especially the hydrophobic sorption mechanism. However, other sorption mechanisms are also possible and K_{OC} of non-ionizable and neutral pollutants may vary among soils, principally for aromatic and heterocyclic compounds, affecting the validity of QSAR assumption (Figure 4).

3.3.2 Analysis of PTF assumptions

The hydrophobic sorption of non-ionizable and neutral pollutants was predicted by PTF models using soil descriptors and always following the same trends: positive and negative correlation with OC and pH, respectively (Kodešová et al., 2015; Singh et al., 2016; Klement et al., 2018; Hu et al., 2022). However, the magnitude of the effect of each descriptor depended on the pollutant.

The sorption of ionic pesticides (anions, cations and zwitterions) in empirical studies in the literature correlated with OC and pH (Skeff et al., 2018; Caceres-Jensen et al., 2019; Loffredo et al., 2019; Meftaul et al., 2020; Meftaul et al., 2021), but observed trends varied among the experimental studies. The same occurred in PTF models, where correlations with OC were positive (Klement et al., 2018; Conde-Cid et al., 2019), negative (Dollinger et al., 2015; Klement et al., 2018) or negligible (Kodešová et al., 2015; Sidoli et al., 2016; De Gerónimo et al., 2018), and other soil variables such as clay content, Fe and Al oxide content, CEC and base-cation saturation were more relevant than OC (Dollinger et al., 2015; Kodešová et al., 2015; Sidoli et al., 2016; De Gerónimo et al., 2018; Klement et al., 2018).

The variability explained by soil or pollutant properties was also variable. In studies including strong acids, the soil variability was negligible (Alfonso et al., 2017) or defined by clay content and specific minerals (Marín-Benito et al., 2017). Additionally, the contribution of minerals, the lack of correlation between sorption coefficients and OC, or the high variability of K_{OC} values for the same pesticide have been used as an indicator that K_{OC} may not always be appropriate for describing the sorption in soils (Cáceres-Jensen et al., 2021; Siek et al., 2021). The same variability has been found in PTF models, where the complexity of the sorption mechanism produced positive and negative trends for (i) clay and OC content (Dollinger et al., 2015; De Gerónimo et al., 2018) and (ii) the presence of phosphorus on soils (Sidoli et al., 2016; De Gerónimo et al., 2018). These cases imply that the sorption process is specific for each pesticide-soil combination, and trends require contextualization before assuming its simplicity or complexity (Figures 4D–F).

The pH-dependent surface charge was a particular soil characteristic impacting the sorption of ionic pesticides. Sorption coefficients of anionic pesticides were explained by soil texture, content of Fe and Al oxides and isoelectric point of soils in experimental studies (Skeff et al., 2018; Caceres-Jensen et al., 2019; Meftaul et al., 2020; Cáceres-Jensen et al., 2021; Meftaul et al., 2021) and PTF models (Sidoli et al., 2016; De Gerónimo et al., 2018). For example, glyphosate sorption was mainly non-hydrophobic and higher in variable charge soils than in permanent charge soils, depending on the isoelectric point and content of Fe and Al oxides (Skeff et al., 2018; Caceres-Jensen et al., 2019; Pereira et al., 2019; Meftaul et al., 2021) (Figure 4D versus 4E). This behavior made K_{OC} not appropriate to describe the glyphosate dynamics (Skeff et al., 2018; Caceres-Jensen et al., 2019).

Finally, articles that studied OV [exp] showed that the sorption coefficients and nonlinearity (1/n ≠ 1) of sorption were affected by the use of pure versus mixed pesticides (Sousa et al., 2018) and by temperature (Kaur et al., 2018) during the sorption study of non-ionizable, weak base and strong acid pesticides. Similarly, PTF models included environmental and methodological conditions during the data splitting or as predictor variables to minimize those impacts.

3.3.2.1 Key insights

Sorption followed diverse trends depending on the acid-base activity of pollutants and kind of soil (permanent and variable charge soils). PTF models are applicable for predicting hydrophobic sorption, conceptually linked to the QSAR assumption, but soil properties (OC, pH) had different impacts (e.g., correlations) depending on the pollutant. Furthermore, PTF models can represent sorption mechanisms in specific scenarios beyond QSAR assumption.

4 Discussion

In this section we discuss our findings, considering requirements for developing and unifying QSAR and PTF models from an empirical perspective, including recommendations for scientific and regulatory decisions. We used headers to simplify the understanding of our proposals.

4.1 Requirements for developing and applying predictive models

Based on findings from the literature, we found three topics required for applying predictive models for regulatory purposes: (i) an explicit connection between simplification strategies (QSAR and PTF assumptions, Figure 4) and the representational value of data, (ii) tools and procedures for validating predictive models and their applicability, and (iii) practical needs covered by predictive models for regulatory purposes.

4.1.1 Representational value

Production, collection and treatment of data determine their representational value and potential use as evidence of the phenomenon they are intended to represent (Leonelli, 2019). Therefore, QSAR and PTF assumptions (Figure 4; Section 3.1) should be evaluated and validated to minimize biases. For instance, the idea that the hydrophobic sorption mechanism is generalizable (QSAR assumption) might be enhanced by the distribution of acid-base activities (Tables 2, 3), where most of the current information in the literature is focused on sorption mechanisms independent or only slightly dependent on pH. Moreover, most of the pesticides studied were aromatic (Supplementary Figure S1), which mainly present hydrophobic mechanisms despite other interactions (e.g., polar). In this sense, we recommend validating the assumptions based on the empirical findings applied to the dataset used to develop predictive models.

We can further generalize the QSAR assumption to the following statement: "Predictions can be extrapolated among soils when they share an unspecific sorption mechanism occurring in a unique and common soil component". If that soil component is OC (see Figures 4A–C, F), and the soil variability (including environmental and methodological conditions) is so low that it can be neglected compared to the variability among pollutants, then it is possible to quantify an average sorption coefficient value per pollutant and create QSAR models.

The notion of generalization has three implications: (i) Both QSAR and PTF can share data (see Figures 4C, F, belonging to different kinds of model despite being equivalent), (ii) the generalization of QSAR assumption may help to develop new QSAR models or simplify PTF models, e.g., if the common soil component is different than OC, and (iii) all models (even QSAR) are applicable to soils with properties similar to those used during the data collection and treatment, so soils should necessarily be included in the AD.

4.1.2 Validation tools

The validation of predictive models should consider their representational value and statistical parameters. Both kinds of validation are necessary and complementary, addressing methodological and environmental conditions affecting the sorption coefficients and isotherm shape (as PTF models) and giving the models a statistical and reproducible quality in accordance with the OECD principles (as QSAR models).

Validation should be considered in all steps, such as data splitting (e.g., splitting pure and mixed pollutants into different datasets, and afterwards dividing them again into their respective training and test sets) or selection of predictor variables (e.g., proposing them based on the sources of variability and then evaluating different algorithms to produce the mathematical equation).

For regulatory decisions, the validation process should improve the applicability of predictive models in environmental scenarios of concern with relevant but rarely studied sources or variability, especially in agricultural contexts where (i) commercial formulations may contain mixtures, (ii) pesticides can be added in previously polluted soils, or (iii) the seasonality could produce relevant temperature variations.

From an institutional perspective, only QSAR models are used or promoted as reliable tools (OECD, 2014; Nolte and Ragas, 2017; Chi et al., 2018; Kar et al., 2018; Thomas et al., 2019), probably due to the generalizability and simplicity of these models in comparison with PTF models, which depend on local conditions as well as specific procedures and predictor variables. Following the QSAR assumption (Figure 4), the OECD assumes that sorption coefficients are physicochemical properties of pollutants (Kar et al., 2018) so its principles have more impact on statistical validation than the outcome selection (always K_{OC}). However, we found empirical studies that contradict the QSAR assumption, which might explain why current QSAR models for predicting soil pollution are not included in REACH Analysis of Alternatives reports for authorization of active substances (Chinen and Malloy, 2020).

Considering the above, procedures derived from PTF models may strengthen the application of OECD principles P1 and P5 (Figure 3) by giving a mechanistic context, while statistical tools used in QSAR models support the principles P2, P4 and P3. In this sense, future predictive models could combine both practices and be mechanistically and statistically reliable from an institutional perspective.

4.1.3 Usability for regulatory purposes

The AD of predictive models represents the variability boundaries in which the model was built (e.g., structural diversity, methodological and environmental conditions, predictor variables), required to interpolate new cases, avoiding the uncertainty of extrapolations. In this sense, applicability depends on the dataset. However, it is usually impossible to determine sorption mechanisms in real systems. Notably, sorption experiments are made in ideal conditions, where sorption is isolated from competitive processes such as biological (Kaur et al., 2018; Silva et al., 2018; Skeff et al., 2018; Xu et al., 2020; Beringer et al., 2021; Chen et al., 2021; Siek et al., 2021) or chemical degradation (Góngora-Echeverría et al., 2019; Loffredo et al., 2019; Zhao et al., 2020; Beringer et al., 2021). Furthermore, methodological conditions are not representative of real conditions, such as soil:solution ratio <1 (saturated soil), the usage of a background solution in all studies, controlled pH and temperature (e.g., OV [exp]), or the scarce connection between the interval of concentrations used to quantify sorption coefficients and the field dosages (only done in (Pavão et al., 2022; Mosquera-Vivas et al., 2018; Dos Santos et al., 2019; das Chagas et al., 2020. Predictive models should therefore be used cautiously. What they represent is useful for researchers but not necessarily reflective of regulatory needs, meaning that a clearly defined AD (P3, Figure 3) is necessary but not sufficient to ensure regulatory purposes.

The representational value is key to connect data with real scenarios and establish the correct questions that predictive models can answer for making decisions (Figure 1). For example,

it is inappropriate to use sorption coefficients (quantified in equilibrium condition) to represent non-equilibrium scenarios such as environmental fate at non-saturated or variably saturated conditions, e.g., during irrigation, heavy rain, or flooding. However, scientists and environmental entities could use those sorption coefficients to estimate the maximum sorption (at equilibrium) and then the minimum transport of pollutants in ideal conditions. Furthermore, the relevance of sorption with respect to transport in the long term may help to understand the implications of using predictive models for sorption in a specific site or situation.

Additionally, the usability of predictive models depends on their simplicity when used by non-experts, especially when they present predictor variables that are easy to understand and quantify (Berthod et al., 2017; Conde-Cid et al., 2020). If QSAR and PTF models are equally applicable in a hypothetical situation, then QSAR models are easy to implement due to the use of molecular and theoretical descriptors, whose quantification is independent of local conditions, while PTF models have simpler interpretations due to their contextualized predictor variables, helping to understand the meaning of predictions.

4.2 Unifying QSAR and PTF models backgrounds

Following from the above, it is difficult to know *a priori* how complex the sorption is, and it is difficult to determine sorption mechanisms when several pollutant-soil interactions are possible (see Figures 4D, E). In more complex scenarios, even interactions among soil components or pollutants, such as OC-oxide minerals and multilayer sorption (linearity coefficient $1/n > 1$) (Alfonso et al., 2017; Marín-Benito et al., 2017; Pose-Juan et al., 2018; Sousa et al., 2018; Caceres-Jensen et al., 2019; Góngora-Echeverría et al., 2019; García-Delgado et al., 2020; Cáceres-Jensen et al., 2021; Meftaul et al., 2021) are possible. However, we found empirical trends that (i) are available through comparative analysis from the literature, (ii) are relatively easy to identify from empirical findings, and (iii) are sufficient to recognize, broadly speaking, how much complexity an overall sorption coefficient is representing. In this sense, we propose the use of three empirical correlations to identify what kind of predictive model is applicable in a case-by-case analysis:

C1. A positive correlation between the sorption coefficient and the percentage of the neutral (uncharged) form of pollutants (100% if the pollutant is non-ionizable).

C2. An exclusive and positive correlation between sorption coefficients and OC (i.e., lack of correlation with other soil properties).

C3. Positive correlations between hydrophobic OC components and sorption coefficients.

4.2.1 Interpretation

These three previous correlations are presented from general to specific. We initially assume that any sorption trend is possible within a dataset. Then, we may simplify the development of predictive models without losing representational value depending on the findings about C1, C2 and C3. If C1 is true, then the sorption is mainly non-ionic (see Figures 4A–C, E, F). If C2 is true, then OC is the most relevant sorbent (see Figures 4A–C, F). Finally, if C3 is also true, then sorption may be represented as hydrophobic on OC (impossible to determine from Figure 4, because it involves the OC composition).

In this sense, an agreement with C1, C2 and C3 represents the hydrophobic sorption assumed in QSAR models, while the non-compliance with any correlation involves the relevance of non-hydrophobic sorption mechanisms, which account for mechanistic diversity (i.e., evidence of several kinds of pollutant-sorbent interaction) instead of fixed statements (QSAR and PTF assumptions, Figure 4). Additionally, these correlations are sensitive to different acid-base activities, chemical classes and soils. Finally, they may be validated experimentally through (i) the changes in sorption of pollutants on each soil at different pH values (C1), (ii) sorption observed in isolated non-organic components of soils and detection of multicollinearity with OC in case other correlations are detected (C2), and (iii) sorption trends on isolated specific OC components, e.g., aliphatic-C, aromatic-C (C3).

Note that C1 and C3 can be fulfilled without C2. This case implies that (i) the main sorbent is OC, but the correlations are hidden by changes in the OC composition among sorbents or interactions between OC and other soil components (e.g., Figures 4C, F *versus* Figure 4A, B if OC interacts with minerals), or (ii) other sorption mechanisms are relevant, but were eliminated during the experimental procedure to assess C3 (Figure 4E could potentially be an example). To minimize this or other sources of uncertainty or misrepresentations of the sorption coefficient, the corroboration of correlations should follow the specific order: first C1, then C2, and finally C3.

4.2.2 Connection with predictive models

If C1, C2 and C3 are true, then OV [pollut] is sufficient to represent the variability among sorption coefficients (i.e., SV [soil], SV [treat], SV [spatial], and OV [exp] are negligible in the dataset). Therefore, QSAR models are valid approaches to represent the variability within the dataset. On the other hand, PTF models are representative of the dataset if OV [pollut] is negligible (e.g., only one pollutant is analyzed) and SV [soil], SV [spatial], OV [exp] and SV [treat] can be fully explained by physicochemical soil properties. Finally, researchers should use PTF models or hybrid models including soil and pollutant properties as predictor variables when correlations C1, C2 and C3 are false or partially true.

4.2.3 Conditions

Model development (Figure 1) should consider whether the data meet the correlations C1, C2 and C3 to decide an adequate strategy (QSAR, PTF). Afterwards, outcome selection, data treatment, proposal of predictor variables and AD should include the following empirical information of the studies used for obtaining the data: (i) physicochemical properties of pollutants and soils, (ii) methodological and environmental conditions, and (iii) shape of the isotherm. The third topic is especially relevant for QSAR models (i.e., C1 to C3 are met) built from data with different sorption shapes, so the sorption coefficients associated with one

pollutant are similar in magnitude but have different interpretations. Finally, the model implementation (Figure 1) should judge if their scenario of concern is included in the model AD (e.g., inclusion of soil samples from different depths, use of fertilized soils).

4.3 Recommendations

In this section, we propose best practices for developing, interpreting, and using current and future predictive models, especially QSAR models due to their institutionalization.

4.3.1 Using empirical information for developing predictive models

The reliability of predictive models and their connection with representational value of data may improve by using sources of variability and our proposed correlations jointly in various stages of the development of predictive models (Figure 3), helping and complementing OECD and REACH guidelines through the following approaches and steps.

4.3.1.1 Exploring sorption mechanisms

Sources of variability can improve the connection between representational value of data and predictive models when used to (i) explore the correlations C1 to C3 (SV [soil]), (ii) detect properties of pollutants and soils affecting sorption (OV [pollut], SV [soil]), and (iii) describe the impact of methodological and environmental conditions in the sorption process in specific contexts (e.g., climate, agricultural practices; OV [exp], SV [treat]). As a result, empirical findings may guide the selection of suitable approaches (QSAR or PTF), outcomes and predictor variables to avoid misrepresentations (e.g., unexplored or underrepresented but relevant sorption mechanisms).

4.3.1.2 Scoping the model

We suggest having a clear objective according to the expected performance and applicability of predictive models, especially the scale and degree of specificity. For instance, variable charge soils (Figures 4A, D) are not common in the literature and their sorption behavior may be hidden among the most common trends (Figures 4B, C, E, F). However, variable charge soils possess a high agricultural productivity, which makes them relevant from a regulatory perspective, specifically for agriculture-based economies from emerging and developing countries (Caceres-Jensen et al., 2019). Then, a predictive model created from large datasets without a mechanistic treatment of data will have general applicability, making the conventional sorption mechanisms and predictive models less useful to predict and interpret specific and important scenarios (e.g., Figure 4D). In this sense, models that have different scope or address infrequent cases provide information that complements our understanding of the sorption process.

4.3.1.3 Dataset

Predictive models should represent the variability among data in the simplest way possible, considering the available information

under comparable conditions. As an example, changes in sorption coefficients of soil samples at different depths (SV [spatial]) or influenced by different treatments (SV [treat]) were generally explained by changes in the physicochemical properties of soils (e.g., OC content (endogenous + exogenous), kind of OC, pH, salinity) (Khorram et al., 2018; Pose-Juan et al., 2018; Silva et al., 2018; García-Delgado et al., 2020; Siek et al., 2021; Mosquera-Vivas et al., 2018; Sousa et al., 2018; Dos Santos et al., 2019; das Chagas et al., 2020; Marín-Benito et al., 2017) (see Table 2). Thus, they behaved as different (but conceptually connected) soils and could be included in the same dataset without requiring predictor variables accounting for depth or treatment information. Nevertheless, the extent of change in the soil properties varied among pesticides (Marín-Benito et al., 2017; Pose-Juan et al., 2018) and soils (Pavão et al., 2022; das Chagas et al., 2020), indicating that specific pesticide-sorbent and soil-amendment interactions were relevant when SV [treat]+OV [pollut] and SV [soil, treat] were addressed, respectively.

4.3.1.4 Data treatment

The data treatment should consider sources of variability together with statistical tools to decide whether the findings are reliable, especially if the same pollutant was addressed at different levels of complexity and uncertainty (e.g., SV [soil] *versus* OV [exp]). Those cases require a well-defined method to compare studies with different experimental designs to analyze the information and improve our comprehension of the environmental fate.

4.3.1.5 Model performance

Sources of variability are helpful for exploring new predictor variables and improving the AD of models in specific scenarios. The high presence of SV [soil] in the literature may be used to improve the predictability of QSAR models by incorporating soil descriptors based on empirical trends when hydrophobic sorption is dominant but not unique, while SV [treat] and SV [spatial] are helpful for exploring the impact of physicochemical properties of soils on pesticide sorption in agricultural contexts.

4.3.1.6 Scientific interpretation

We recommend explicitly assessing sources of variability within the data and doing so from the simplest to the most complex (e.g., starting with OV [exp], finishing with soil variability). Thus, the first (simple) findings act as a conceptual basis to contextualize and simplify the exploration of later (more complex) trends.

4.3.1.7 Model implementation

Scientific interpretation should guide the decision-making process (Figure 1) when selecting scientific information for regulatory purposes. For example, if the agricultural impact of sorption studies is required to propose, apply or evaluate an environmental policy for soil productivity, then it is necessary to consider SV [spatial] and SV [treat], i.e., models that explicitly included those sources of variability and their interpretation, both related to management practices and application of amendments in agricultural soils. As a result, QSAR and PTF models act as a bridge among scientific and regulatory dimensions, involving complex and diverse decisions to help environmental entities to promote and select strategies for applying adequate models in proper scenarios.

4.3.1.8 Adaptable proposal

Correlations C1 to C3 represent the most probable scenarios we found in the literature, but other simplifications could be applied to non-organic soil components if they are relevant in a subgroup of pollutant-soil systems. To this end, we propose to assess (i) pollutant properties that seem relevant (acid-base activity, chemical class, etc.), (ii) a set of relevant soil components, and (iii) relevant functional groups in the selected soil component. For instance, an alternative sorption mechanism could consider correlations of sorption coefficients and anionic pollutants (alternative C1) when sorption occurs mainly in oxide minerals (alternative C2), specifically in aluminum oxides (alternative C3), which fits with Figure 4D if pollutant-soil interactions involving OC and non-oxide minerals are negligible or less relevant.

4.3.2 How to interpret current QSAR models

It is interesting that current QSAR models are statistically validated and offer mechanistic interpretations, even when their assumptions do not necessarily fit with the empirical findings. We propose three possible explanations (not mutually exclusive) related to (i) subsets of data involving hydrophobic sorption, (ii) the contrast between SV [soil] and OV [pollut], and (iii) overall sorption mechanisms.

4.3.2.1 Subsets of data involving hydrophobic sorption

Let us suppose that non-hydrophobic interactions are relevant (e.g., sorption of glyphosate). In that case, OC and pH do not necessarily correlate with sorption coefficients. Moreover, correlations may be positive or negative depending on the pollutant-soil interaction. However, correlations C1 to C3 might be applicable in a subset of data, given specific experimental conditions (e.g., inclusion of ionizable compounds in their neutral form, quantification of average K_{OC} values based in soils where sorption coefficients and OC correlates positively). Then, pollutants with non-hydrophobic interactions may be included within a diverse set of molecules for developing QSAR models.

From a QSAR perspective, sorption is independent of soils and therefore, QSAR models are assumed to be generalizable (see their assumption, Figure 4). In this case, the extrapolation of the subset of data used for developing the model as if they represent the entire dataset (or available information from the literature) produces a hasty generalization fallacy, with the consequent risk of bias when making decisions in soils whose properties were not considered in the subset of data.

The data selection process may help us to address this issue. For example, a wide interval of K_{OC} values among soils has been observed for the same pollutant when sorption involves different mechanisms (Skeff et al., 2018; Caceres-Jensen et al., 2019; Cáceres-Jensen et al., 2021). If this occurs, data will be chosen from a subgroup that minimizes variability, reducing the diversity of soils where the predictive model is applicable.

Data selection should be described in terms of soil physicochemical properties instead of minimization of the standard deviation only. Otherwise, this practice may support the belief that sorption is strictly hydrophobic and unexplained variability is attributable to incorrect experimental values instead of other sorption mechanisms (Olguin et al., 2019). In this scenario, the explicit description of mechanistic limitations should help

environmental agencies to use predictive models for regulatory purposes in a narrow but valid group of pollutant-soil systems, based on the methodological and environmental conditions used to develop the model.

4.3.2.2 Soil *versus* pollutant variability

In the literature, both soil and pollutant properties produced changes in sorption coefficients. Furthermore, most of the empirical studies were focused on variability among soils, with only a few addressing different pesticides (SV [soil] *versus* OV [pollut]) (see Table 2). However, no study contrasted both sources of variability.

We analyzed two studies with non-normalized sorption coefficient values at comparable conditions ($R^2 \geq 0.95$, same units) addressing SV [soil] and OV [pollut] for >2 soils and >2 pesticides (Agbaogun and Fischer, 2020; García-Delgado et al., 2020).

We calculated five $K_{F(pest)}$ (phenylurea herbicides) and eighteen $K_{F(soil)}$ (alfisols, inceptisols and entisols) values based on findings in the literature (Agbaogun and Fischer, 2020). The obtained COV were 46 ± 6% for $K_{F(pest)}$ and 52 ± 4% for $K_{F(soil)}$, with OV [pollut] slightly higher than SV [soil]. Additionally, this study found a correlation between sorption coefficients and OC (Agbaogun and Fischer, 2020), suggesting that normalize K_F to OC (i.e., K_{OC}) reduces the soil variability. When we normalized K_F (Agbaogun and Fischer, 2020), the new COV values were 32 ± 6% for $K_{OC(pest)}$ and 53 ± 7% for $K_{OC(soil)}$, increasing the relevance of OV [pollut] *versus* SV [soil].

Another study quantified the sorption of four herbicides in two soils, four amendment materials, and the amended soils (García-Delgado et al., 2020). We quantified two $K_{F(pest)}$ per pesticide considering (i) the untreated and treated soils, and (ii) the isolated amendments. We also quantified fourteen $K_{F(soil)}$ (2 control soils + 4 × 2 amended soils +4 isolated amendments).

Considering soils (control + amended), the obtained COV were 47 ± 24% and 87 ± 14% for $K_{F(pest)}$ and $K_{F(soil)}$, respectively. Additionally, COV values for isolated amendments (excluding sewage sludge, that showed a different behavior) were 22 ± 9% and 56 ± 9% for $K_{F(pest)}$ and $K_{F(soil)}$, respectively. The relevance of OV [pollut] is explained by the different chemical classes of herbicides studied, while the low variability in SV [treat] is related to a common sorption mechanism on amendments (hydrophobic sorption on aliphatic and aromatic carbon) (García-Delgado et al., 2020).

The applicability and performance of QSAR models increase when (i) SV [soil] or COV value of $K_{F(pest)}$ are minimized (e.g., normalizing sorption coefficients to soil properties), and (ii) OV [pollut] or COV value of $K_{F(soil)}$ are maximized. Therefore, the variability among sorption coefficients is better explained by changes in the molecular structure of pollutants than by soil properties (OV [pollut] > SV [soil]), which supports the assumption of QSAR models (Figure 4). Otherwise, PTF (OV [pollut] < SV [soil]) or hybrid models (OV [pollut] ~ SV [soil]) become relevant. From studies one and 2, OV [pollut] > SV [soil] when (i) sorption coefficients partially or completely follow the correlation C2 and are then normalized to the corresponding soil properties, or (ii) the sorbents share similar properties due to the treatments, making their sorption mechanisms more similar among sorbents.

4.3.2.3 Overall sorption mechanisms

A third option is that QSAR models represent unrealistic but useful overall trends using average values as outcomes. Consider the following two studies.

A study quantified the sorption of four herbicides in four Mexican soils (Alfonso et al., 2017). We quantified $K_{F(pest)} = 2, 0 \pm 0, 3$ ($\mu g^{1-1/n} mL^{1/n} g^{-1}$) for sulfotep considering all the soils, and $K_{F(soil)} = 2, 8 \pm 0, 5$ ($\mu g^{1-1/n} mL^{1/n} g^{-1}$) for a soil from Chablekal, using two structurally similar pesticides (sulfotep and dimethoate) (Alfonso et al., 2017). The low COV (13% and 16%, respectively) suggests that the use of average values based on similarities to reduce or even neglect the variability is valid for both pesticides and soils (all soils behave as one unique sorbent, while both pesticides behave as one unique pollutant). In this case, the structural differences between both pesticides were not enough to produce an important change on sorption. Thus, both pesticides present the same sorption coefficients when used in a QSAR model.

The opposite situation occurs when the structural variability produces important changes on sorption. From another study involving five pesticides and 18 soils (Agbaogun and Fischer, 2020), we obtained similar $K_{F(pest)}$ values for pesticide with similar structure, such as diuron and linuron (9 ± 3 and 11 ± 5 ($mg\,kg^{-1})(mg\,L^{-1})^{-1/n}$, respectively), or monuron and isoproturon (4 ± 2 and 2 ± 1 ($mg\,kg^{-1})(mg\,L^{-1})^{-1/n}$, respectively). Additionally, we calculated $K_{F(soil)}$ values and observed a variability from 4 ± 2 (Ibd soil, alfisol) to 16 ± 8 ($mg\,kg^{-1})(mg\,L^{-1})^{-1/n}$ (Uib soil, inceptisol). Interestingly, $K_{F(pest)}$ and $K_{F(soil)}$ values correlated positively with lipophilicity of pesticides (e.g., $\log K_{OW}$) and the OC content, respectively, probably due to hydrophobic sorption. This supports the findings from QSAR models, where the normalization of $K_{F(soil)}$ to OC makes sorption independent of soils, while $K_{F(pest)}$ is described exclusively by hydrophobic molecular descriptors.

Similarity among pollutants and soils within the dataset affects their variability and mechanistic interpretation. If sorption is generally represented by one overall sorption mechanism, then the use of average values reduces the variability. Moreover, the normalization of sorption coefficients to relevant soil properties (i.e., correlation C2) makes their variability dependent on pollutant properties (case 2). In this scenario, QSAR models have an interpretation and physicochemical meaning, despite their conceptual issues: they represent a sum of unknown trends with compensatory effects that hide specific sorption mechanisms and methodological differences, showing general trends that do not represent local pollutant-soil interactions but allow to approximate them around a probable value. This might explain the unclear impact of some molecular descriptors when complex sorption mechanisms appear (Rybacka and Andersson, 2016). Therefore, these QSAR models cannot predict sorption coefficients in local contexts and should be useful as exploratory analysis prior to the screening step in risk assessment.

4.4 Limitations

Regarding our findings, the main limitation is related to the heterogeneity of information, affecting the extrapolation of our findings and our conceptual proposal in three ways: (i) sources of variability, (ii) distribution of data, and (iii) scarcity of information.

SV [spatial] and OV [exp] involve the study of several samples, which caused authors to simplify logistics, mainly by using one-point sorption coefficients and/or assuming an equilibrium time of 24 h (Figure 5). As a result, we excluded most of these articles from our review (Figure 5), affecting the confidence of the findings for these sources of variability.

If we consider all combinations in which SV [soil] and OV [pollut] were present (SV [soil], SV [soil, treat], SV [soil, spatial] or SV [soil, treat, spatial] together with OV [pollut], OV [pollut, exp]), we find that <20% of the articles studied SV [soil] and OV [pollut], but they covered >60% of the pesticides (5 articles, 27 pesticides). Therefore, the impact of SV [soil] and OV [pollut] might be overrepresented.

Absent sources of variability such as SV [treat, spatial] and those that involve OV [time] produce uncertainty with regard to the generalizability of simplifications proposed during the data treatment. For instance, we do not know if aging, seasonality, or any other time-dependent source of variability is explained by changes in the physicochemical properties of soils, just like SV [spatial], or have more complex effects on sorption, like SV [treat]. This information might help to understand if predictive models are valid in the long term or require empirical time-dependent descriptors to potentially be used in environmental baseline studies or included in local environmental policies.

Regarding the focus of our analysis, three issues affect the interpretation and extrapolation of our results: (i) selection of pollutants, (ii) correlational analysis of sorption mechanisms, and (iii) strategy to unify QSAR and PTF assumptions.

We used pesticides as a globally relevant organic pollutant model of focus due to their structural diversity and reactivity in combination with the large amount of information available in the literature (Neira-Albornoz et al., 2022). This approach is supported by the equivalent findings from different QSAR models using pesticides *versus* broader ranges of pollutants (Table 1; Section 3.1). However, predictive models and empirical trends for specific non-pesticides compounds might have a different behavior. An example are pharmaceuticals that generally were pH-dependent (PTF models), while pesticides used to be non-ionic (QSAR and literature), affecting the generalizability of our study.

We based our analysis on correlations and connecting both interpretations from theoretical and experimental studies. However, the distribution of data, different experimental designs and collinearity among molecular and soil properties could produce biases when using correlations in the interpretative layer. Biases also have a social explanation, mainly related to global agricultural needs (e.g., the heterogeneous distribution of pesticide usage and the scarcity of studies made on variable charge soils). In this sense, an exhaustive analysis of the context and validity of the empirical trends on a case-by-case basis should minimize biases and oversimplifications of sorption mechanisms.

We proposed hybrid models involving QSAR and PTF assumptions. Considering the lack of mixed models and the lack of experimental studies combining SV [soil] with OV [pollut], our analysis was qualitative. Future research could include molecular

and soil descriptors to quantitatively address the feasibility of our proposal and the improvement in explanatory power (statistically and contextually).

Considering the above, our proposal is a first endeavor to understand the implementation of QSAR and PTF models for decision-making considering the representational value of data and should be tested and adapted in future studies according to new evidence.

5 Conclusion

In this article, we developed a comprehensive contextualization of QSAR and PTF models by evaluating the validity of their assumptions and procedures from an evidence-based perspective using empirical results from the literature. Based on our findings, we proposed the analysis of different (i) requirements, such as the selection of appropriate outcomes and kind of model before developing the model itself, (ii) limitations related to the representational value of data and the simplification strategies followed by QSAR and PTF models, and (iii) applicability conditions at local and global scale (Figure 1). This contextualization involves experimental designs, sources of variability, and methodological procedures used during the quantification of empirical data used in the dataset, whose explicit analysis is key to improve the reliability, interpretation and applicability of predictive models. As a result, our work is intended to help scientists and environmental agencies such as OECD and REACH to (i) adapt the development and use of future predictive models to individual contexts of environmental relevance for regulatory purposes, and (ii) interpret and improve current QSAR and PTF models.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding authors.

Author contributions

AN-A: Conceptualization, Formal Analysis, Investigation, Methodology, Project administration, Validation, Visualization, Writing–original draft, Writing–review and editing. MM-P-M: Validation, Visualization, Writing–review and editing. MG: Validation, Writing–review and editing. AS: Conceptualization, Project administration, Visualization, Writing–review and editing.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fenvs.2024.1379283/full#supplementary-material

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