

Review

Not peer-reviewed version

Research Hotspots and Trend Analysis in Modeling Groundwater Dense Nonaqueous Phase Liquids Contamination based on Bibliometrics

Mengdie Ju , [Xiang Li](#) , [Ruinin Wu](#) , Zuxin Xu , [Hailong Yin](#) *

Posted Date: 10 September 2024

doi: 10.20944/preprints202409.0737.v1

Keywords: dense nonaqueous phase liquids; mathematical model; bibliometrics; multiphase flow; groundwater



Preprints.org is a free multidiscipline platform providing preprint service that is dedicated to making early versions of research outputs permanently available and citable. Preprints posted at Preprints.org appear in Web of Science, Crossref, Google Scholar, Scilit, Europe PMC.

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

Review

Research Hotspots and Trend Analysis in Modeling Groundwater Dense Nonaqueous Phase Liquids Contamination based on Bibliometrics

Mengdie Ju ^{1,2}, Xiang Li ^{1,2}, Ruibin Wu ^{1,2}, Zuxin Xu ^{1,2} and Hailong Yin ^{1,2,*}

¹ Key Laboratory of Urban Water Supply, Water Saving and Water Environment Governance in the Yangtze River Delta of Ministry of Water Resources, Tongji University, Shanghai 200092, China

² State Key Laboratory of Pollution Control and Resource Reuse Research, Tongji University, Shanghai 200092, China

* Correspondence: yinhailong@tongji.edu.cn

Abstract: Modeling dense nonaqueous phase liquids (DNAPLs) contamination in groundwater is challenging because of its multiphase distribution. To understand the research trends of DNAPL modeling in groundwater, a bibliometric analysis was conducted using CiteSpace based on 614 publications from the WoS Core Collection database (1993–2023). The publications were statistically analyzed, and the research hotspots and trends were summarized. The statistical analysis of the publications indicates that: the United States is leading the international research on DNAPL models, followed by China and Canada; collaboration between countries and disciplines in this field needs to be strengthened. The summary of keyword clustering and burst detection reveals that: the current research hotspots focus on multiphase flow models, mass transfer models, back diffusion, and practical applications of the models; the research trends are centered on back diffusion mechanisms, characterization of contamination source zones and prediction of contaminant distribution in real-world sites, as well as the optimization of remediation strategies.

Keywords: dense nonaqueous phase liquids; mathematical model; bibliometrics; multiphase flow; groundwater

1. Introduction

Dense nonaqueous phase liquids (DNAPLs) refer to a class of organic contaminants that are denser than water and poorly soluble in water, existing in groundwater as a non-aqueous phase. Typical DNAPLs include chlorinated organic solvents[1], creosote[2], and polychlorinated biphenyls (PCBs)[3]. Once DNAPLs infiltrate the subsurface, they can persist for extended durations due to their resistance to biodegradation. During this time, they slowly dissolve into the flowing groundwater and form an extensive contamination plume downstream. Meanwhile, the dissolved DNAPLs gradually seep into the low-permeability layers and become a potential secondary pollution source after the depletion of the original source, thereby keeping the DNAPL concentrations in the plume above the maximum contaminant level (MCL)[4]. Given the toxicity of DNAPLs and their potential health risks to humans[5], the remediation of groundwater DNAPL contamination has become an urgent issue that needs to be addressed.

Various remediation technologies have been employed to remove DNAPL contamination, such as surfactant-enhanced aquifer remediation (SEAR)[6,7], in-situ chemical oxidation (ISCO)[8,9], and in-situ bioremediation[10]. While remediation technologies are the primary means of pollution control, modeling is also essential to ensure the effectiveness of remediation efforts due to the invisibility of DNAPL distribution. Therefore, modeling DNAPL contamination has consistently been a focal point of interest for scholars in the field of groundwater environmental studies. However, the research on DNAPL models varies in focus, and there is a lack of comprehensive statistical analysis of the research outcomes at a macro scale. Consequently, it is essential to systematically

review the hotspots in the field of DNAPL models to accurately grasp the research directions and evolving trends.

Bibliometric analysis, as a method for systematically and quantitatively analyzing scientific literature, provides reliable data support and criteria for scientific research, making it an indispensable tool in the research field. Therefore, this study conducted a statistical analysis of nearly 30 years of literature related to DNAPL models, following a bibliometric process[11]. The study also performed a visual presentation of the research status and trends, aiming to provide insights and references for future study.

2. Methodology

2.1. Database Selection

The WoS Core Collection database was selected as the primary data source for this study. A total of 681 publications were retrieved over the 30-year period from January 1, 1993, to December 31, 2023, taking “DNAPL” and “model” as the search topics. After filtering for document type as “Article” and further screening and deduplication, 614 publications remained for research analysis.

2.2. Bibliometric Indicators and Tools Used

A general analysis of the publication volume of the 614 articles was first conducted, and the data was plotted using Origin software to gain an initial understanding of the overall trends in DNAPL modeling research. The publishing countries, institutions, journals, and keywords over the past 30 years (1993-2023) were then statistically analyzed and mapped using CiteSpace 6.3.R1[12] as the primary tool for bibliometric analysis.

The CiteSpace parameters were set as follows. The time slice was set to 1 year. For the co-citation analysis of different countries, institutions, and journals, the node types were set to “Country”, “Institution”, and “Cited Journal”, respectively, with the k-value in the g-index parameter set to 25 for each. For the keyword clustering analysis, the node type was set to “Keyword”, with the g-index parameter k value set to 20. This adjustment was made to reduce the number of nodes in the map, preventing it from becoming overly complex and difficult to interpret.

3. Findings of Bibliometric Analysis

3.1. Analysis of The Publication Volume

The annual publication volume and its changes can reveal the development status of a research field and its current level of attention. From 1993 to 2023, the total number of publications related to DNAPL models accumulated each year (Figure 1). During the initial budding stage (1993-1999), the annual publication volume was generally below 10 papers. However, 1998 saw a notable increase, with 20 papers published. During the rapid development stage (2000-2010), the annual publication volume gradually increased and stabilized at 20-30 papers per year from 2002 onward, indicating sustained academic interest. During the continuous breakthrough stage (2011-2023), the annual publication volume fluctuated significantly. Publication numbers were the lowest in 2011 and 2016, with only 12 papers, while 2023 saw a breakthrough with 40 papers published. From the above, it is clear that there is still room for further exploration in the research of DNAPL models.

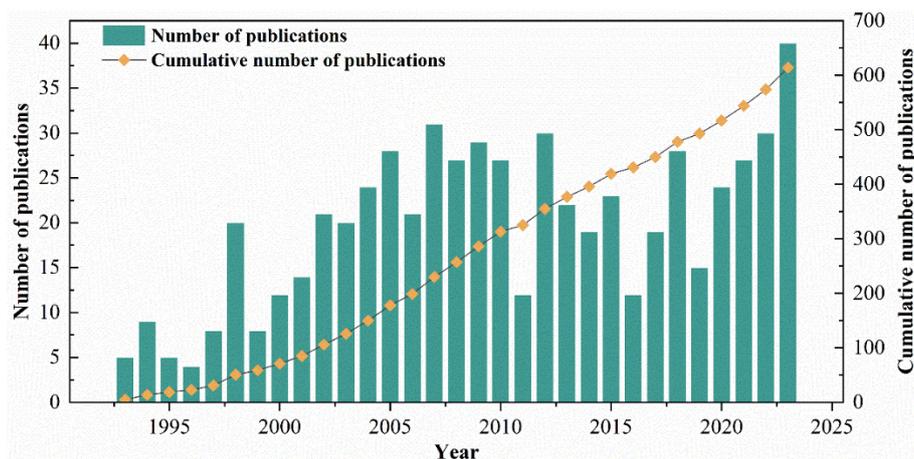


Figure 1. Variation in publications on DNAPL models from 1993 to 2023

3.2. Analysis of The Leading Countries

The national collaboration network reveals the importance of individual countries and the interconnections between multiple countries in a specific research field. The co-citation network of collaborative countries (Figure 2), based on WoS Core Collection data, revealed that 48 countries have published research on groundwater DNAPL contamination modeling. The countries with 10 or more publications are listed in Table 1.

In terms of publication volume, the United States leads the field of groundwater DNAPL contamination modeling with 307 publications, followed by Canada with 112. This is related to the fact that most DNAPL-contaminated sites are located in the United States and Canada[13]. China ranks third with 82 publications but started later than the United States and Canada, with relevant research beginning in 2003. Among the top ten countries by publication volume, the United States, Canada, Germany, and the Netherlands started research early, while most of the other countries began their work after 2000.

Centrality is an indicator that reflects the importance of a country within a collaboration network. A centrality greater than 0.1 indicates that the country plays a crucial role in advancing the research field. In terms of centrality, the United States has a centrality of 0.95 in the national collaboration network, significantly higher than any other country. England follows with a centrality of 0.23. Other countries with a centrality greater than 0.1 include China (0.18), France (0.16), Turkey (0.16), Greece (0.15), and Scotland (0.11). The above countries with high centrality are marked with a purple outer ring in Figure 2. Although Canada has a high publication volume, its influence is relatively weaker, with a centrality of 0.09.

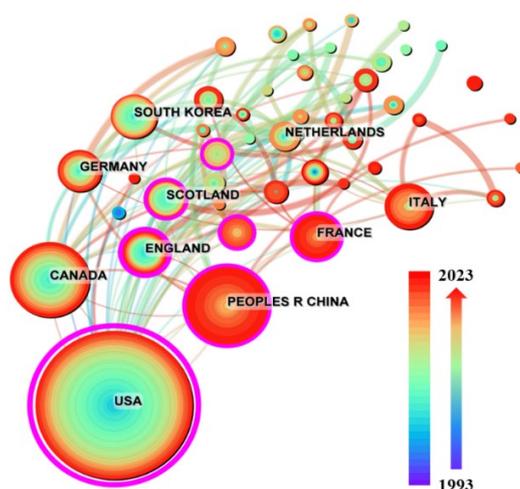


Figure 2. Co-citation network of collaborative countries in DNAPL models**Table 1.** List of Countries with 10 or more publications from 1993 to 2023.

Country	Number of Papers	Centrality
USA	307	0.95
CANADA	112	0.09
PEOPLES R CHINA	82	0.18
FRANCE	33	0.16
ITALY	22	0.04
SOUTH KOREA	21	0.02
ENGLAND	20	0.23
GERMANY	20	0.05
SCOTLAND	16	0.11
NETHERLANDS	14	0.03
AUSTRALIA	13	0.01
TURKEY	11	0.16
GREECE	10	0.15

Overall, the United States leads in DNAPL contamination modeling. This is due to its advanced chemical industry, which results in more contaminated sites and draws significant scholarly attention, along with its strong economy providing substantial support for related research. Therefore, referencing American scholars' research can offer valuable guidance for mastering and applying DNAPL models.

3.3. Analysis of The Leading Institutions

A total of 365 institutions have published research related to DNAPL models, according to the analysis of selected publications. The top 25 institutions with more than 10 publications were selected to create a co-citation network map (Figure 3) for visual analysis.

In terms of timeline and publication volume, the United States Department of Energy (DOE), Queen's University, and the University of Waterloo are the top three institutions with earlier research and higher publication numbers, with 38, 29, and 27 papers, respectively. Moreover, they continue to produce relevant research in recent years. China and France started later but have recently focused more on DNAPL model research, achieving notable results. In DNAPL contamination modeling, China is represented by Nanjing University and Jilin University, with 24 and 22 publications, respectively.

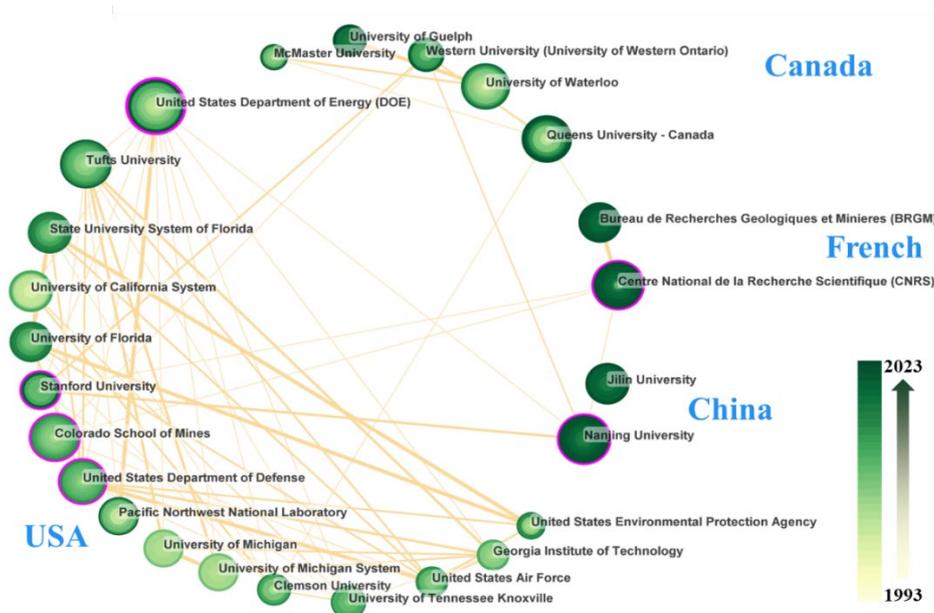


Figure 3. Co-citation network of collaborative institutions in DNAPL models

Spatially, it is clear that most research institutions with higher output are located in the United States, followed by Canada, which aligns with the earlier analysis of publication by country. In contrast, only Nanjing University and Jilin University stand out in DNAPL model research in China, indicating that DNAPL models are not yet widely adopted. Additionally, there is significant collaboration between U.S. institutions, but international collaboration remains noticeably limited. Therefore, future research should focus on two key areas: (1) increasing global awareness of groundwater DNAPL contamination and promoting the application of DNAPL models; (2) enhancing international collaboration to leverage research experience and drive innovation in DNAPL modeling technologies.

3.4. Analysis of The Dominant Journals

The top 10 journals ranked by citation counts in DNAPL model research from 1993 to 2023 are listed in Table 2. The top three journals by citation count are *Journal of Contaminant Hydrology*, *Water Resources Research*, and *Environmental Science & Technology*, which also lead in publication volume in this field. The publication journals indicate that DNAPL model research can be divided into two categories. One focuses on areas like “environment”, “chemistry”, and “materials”, with representative journals such as *Environmental Science & Technology*, *Journal of Hazardous Materials*, and *Chemosphere*, emphasizing the exploration of DNAPL reaction mechanisms and generally having higher impact factors. The other category leans toward “groundwater”, “hydrogeology”, and “pollution distribution and remediation”, represented by journals like *Journal of Contaminant Hydrology*, *Water Resources Research*, and *Groundwater*, focusing on the simulation and prediction of DNAPL pollution evolution. In the top ten journals, most publications are related to the latter category, showing that DNAPL contamination modeling with a focus on hydrogeology is the primary area of research.

Table 2. List of the top 10 cited journals from 1993 to 2023.

Journal	Number of Citations	Number of Papers	Proportion %	IF (2024)
Journal Of Contaminant Hydrology	514	165	26.87	3.5
Water Resources Research	512	57	9.28	4.6

Environmental Science & Technology	444	38	6.19	10.8
Groundwater	349	17	2.77	2
Advances In Water Resources	312	30	4.89	4
Ground Water Monitoring And Remediation	232	16	2.61	1.8
Journal Of Hydrology	186	20	3.26	5.9
Journal Of Hazardous Materials	183	13	2.12	12.2
Transport In Porous Media	158	12	1.95	2.7
Chemosphere	120	10	1.63	8.1

Notably, most journals publishing DNAPL model literature have relatively low impact factors, likely due to the specialized and independent nature of the research. As shown in Figure 4, DNAPL model research is mainly concentrated in fields such as “Ecology, Earth, Marine”, “Physics, Materials, Chemistry”, and “Mathematics, Systems, Mathematical”, with limited interdisciplinary integration, resulting in restricted attention and impact.

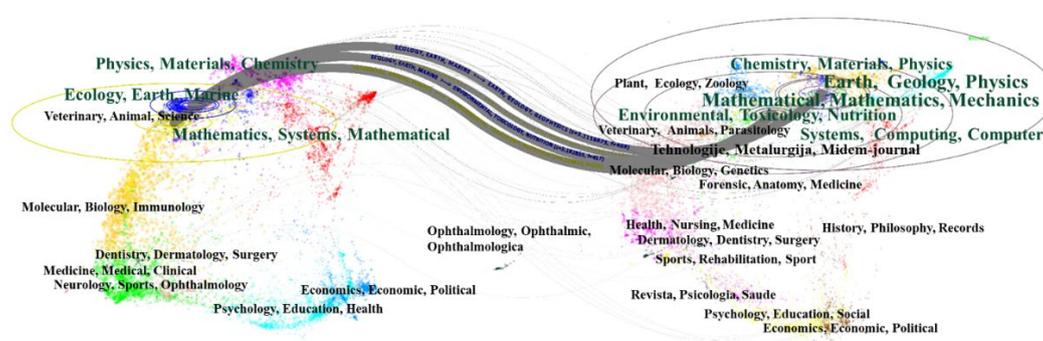


Figure 4. Knowledge map of periodical double graph superposition for WoS publications from 1993 to 2023 (The left area represents the citing journal clusters of knowledge frontiers, while the right area represents the cited journal clusters of knowledge foundations. The curves represent citation paths, with their thickness indicating the frequency and intensity of knowledge flow between journals. The size of the ellipses reflects each journal’s publication volume and author count. More papers lengthen the vertical axis, while more authors lengthen the horizontal axis).

3.5. Analysis of Research Hotspots and Trends Based on Keyword Clustering

3.5.1 Research Hotspots in modeling DNAPL contamination

The DNAPL model framework can be broadly divided into three parts: multiphase flow model, mass transfer model, and dissolved phase transport model. The model can be integrated with experimental findings to clarify DNAPL migration in groundwater and predict contamination distribution, aiding site remediation efforts. To better understand the research status in DNAPL contamination modeling, a keyword co-occurrence analysis was conducted, followed by clustering using the log-likelihood ratio (LLR) algorithm to reveal current research hotspots. The keyword clustering yielded a Q value of 0.4169 and an S value of 0.7499 ($Q > 0.3$ indicates significant structure; $S \geq 0.7$ indicates full reliability). The 10 clusters related to DNAPL models (Figure 5) highlight five prominent keywords each and exhibit interconnections between clusters.

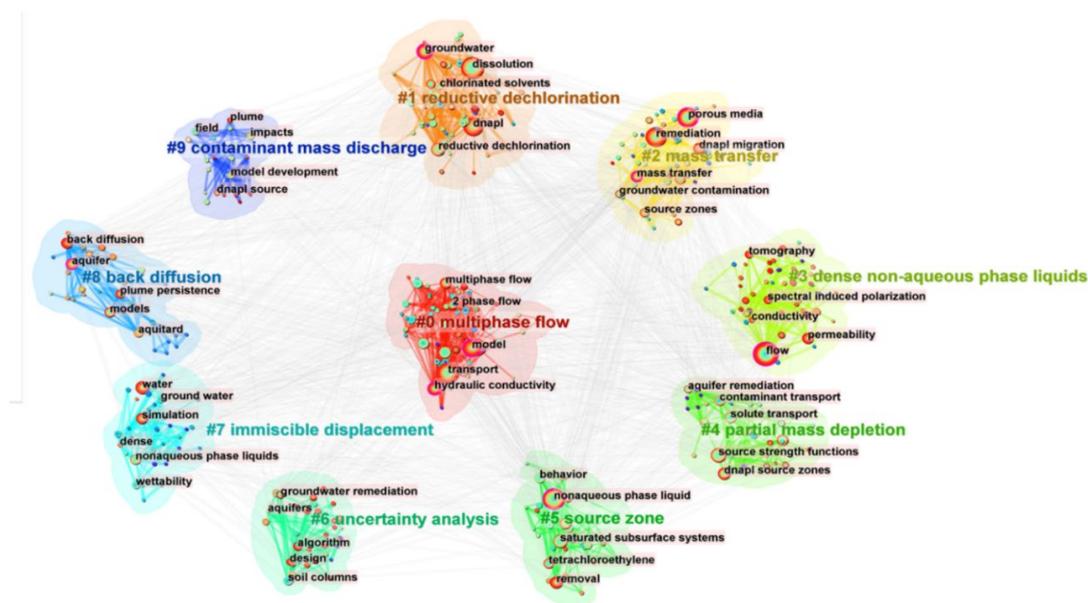


Figure 5. Co-occurrence network of keywords in DNAPL models from 1993 to 2023

Cluster 1 (#0 multiphase flow): The multiphase flow model describes DNAPL multiphase migration and is the foundation of DNAPL modeling research. Due to their high density and low viscosity, DNAPLs infiltrate deep into the subsurface, pass through the unsaturated zone, contaminate aquifers, and accumulate on the aquitard, forming pools[14]. In this process, DNAPLs remain as a NAPL phase and slowly dissolve into the groundwater, becoming a source of dissolved DNAPLs. Many researchers use multiphase flow models to simulate this process and determine DNAPL distribution in the source zone. Research indicates that the key factors to consider when setting up multiphase models include pollutant release situations[15-17], aquifer heterogeneity[18-20], constitutive relations representing the permeability-saturation-capillary pressure ($K_{r,N} - S_w - P_c$) correlation[21-23], and groundwater flow velocity[14,24].

Cluster 2 (#1 reductive dichlorination): On one hand, researchers focus on chlorinated organic solvents to enhance reductive dechlorination techniques. F. Fagerlund et al. [25] used experiments and modeling to study the coupled process of PCE dissolution and dechlorination by nanoscale zero-valent iron in DNAPL source zones. On the other hand, given the common occurrence of PCE and TCE contamination sites, most studies focus on simulating and predicting these pollutants[26-28].

Cluster 3 (#2 mass transfer): Understanding the mass transfer mechanism of DNAPLs from the NAPL to the dissolved phase and establishing an appropriate expression is crucial for source-sink terms in plume modeling. A typical empirical rate-limited expression based on dissolution kinetics is:

$$J = \bar{k}a_{nw}(C_s - C) \quad (1)$$

where J is the mass flux of dissolution from the NAPL phase to the aqueous phase, [$\text{ML}^{-3}\text{T}^{-1}$]; \bar{k} is the average mass transfer coefficient at the NAPL-water interface, [LT^{-1}]; a_{nw} is the effective specific interfacial area between the NAPL phase and the aqueous phase, [L^{-1}]; C_s is the equilibrium aqueous phase concentration, also known as the effective solubility, [ML^{-3}]; and C is the aqueous phase concentration, [ML^{-3}].

Numerous studies have focused on optimizing mass transfer coefficients to improve the analysis and mathematical representation of the DNAPL dissolution process[29-32]. These coefficients are then incorporated into solute transport models to achieve accurate estimates of contaminant concentrations near source zones. To enable site-scale simulations, Parker and Park[33] developed an empirical expression for effective mass transfer coefficients under pseudo-steady-state conditions, providing a valuable reference for subsequent research[34-38].

Cluster 4 (#3 dense non-aqueous phase liquids): DNAPLs naturally form a cluster as a research focus. However, it is noteworthy that keywords such as “tomography”, “spectral induced polarization”, and “conductivity” appear under this cluster. This highlights that coupling geophysical multi-source data for DNAPL contamination modeling has become a key area of interest for scholars. Power et al.[39] developed a DNAPL-ERT numerical model by integrating Electrical Resistivity Tomography (ERT). This model calculates the resistivity response to key hydrogeological parameters (hydraulic permeability, porosity, clay content, groundwater salinity and temperature, and air, water, and DNAPL contents evolving with time), which enhances the sensitivity to heterogeneity in DNAPL distribution and soil structure. Kang et al.[40-42] coupled geophysics with DNAPL models and integrated them into various inversion frameworks, which improved source zone characterization.

Cluster 5 (#4 partial mass depletion): Mass depletion refers to the gradual dissolution and eventual depletion of the NAPL phase in the source zone over time. Similar to mass transfer, this cluster describes the conversion of the NAPL phase to the dissolved phase. However, the difference is that the mass transfer model links the multiphase flow model with the dissolved phase transport model, whereas the source strength function, which characterizes NAPL mass depletion, acts as a source term in the dissolved phase transport model. This simplifies the dissolution process in the source zone and reduces model complexity. The source strength function is typically a power-law relationship between the effluent concentration and the remaining DNAPL mass. The source strength function proposed by Falta et al. [43] has been widely adopted:

$$\frac{C_s(t)}{C_0} = \left(\frac{M(t)}{M_0}\right)^\Gamma \quad (2)$$

where $C_s(t)$ and $M(t)$ correspond to the DNAPL concentration in the source zone and the residual DNAPL mass at time t , respectively; C_0 and M_0 are the DNAPL concentrations in the source zone and the residual DNAPL mass at the initial time; and Γ is a model parameter.

Cluster 6 (#5 source zone): This cluster focuses on the inversion and identification of DNAPL source zones in saturated aquifers. China has conducted extensive research in this area, with most efforts focused on improving the accuracy of DNAPL source zone inversion. For example, Kang[40] proposed a joint inversion framework (CVAE-ESMDA) combining a convolutional variational autoencoder (CVAE) with the ensemble smoother with multiple data assimilation (ESMDA). This approach integrates multiple data sources (OHT, downstream DNAPL concentrations, and ERT) to more accurately estimate DNAPL saturation in the source zone. Wang et al.[44] combined the ensemble Kalman filter with an improved butterfly optimization algorithm, improving inversion accuracy and effectiveness.

Cluster 7 (#6 uncertainty analysis): Inversion of DNAPL source or optimization of remediation strategies based on simulation-optimization methods often involves uncertainty, requiring repeated model runs and high computational costs. Therefore, many studies develop surrogate models to reduce computational load and conduct uncertainty analysis. Hou et al.[45] developed an integrated surrogate model based on support vector regression (SVR), kriging, and kernel extreme learning machine (KELM). The homotopy-differential evolution (DE) algorithm was then combined with the surrogate for source inversion and uncertainty analysis, significantly improving identification accuracy. Du et al.[46] developed a fast-running convolutional neural network (CNN) surrogate model to identify the optimal SEAR scheme under uncertainty, improving optimization speed by 99.8% in 3D numerical experiments.

Cluster 8 (#7 immiscible displacement): In DNAPL contamination scenarios, immiscible displacement describes the relative movement between the NAPL and water phases at a small-scale heterogeneous pore level, driven by differences in gravity and viscosity, leading to NAPL displacing water and migrating downward. At the macro level, this corresponds to the multiphase flow described in Cluster 1. However, while multiphase flow simulation based on continuous models can statistically characterize heterogeneity at the macro level, it is difficult to capture the displacement behavior between the NAPL and groundwater phases at the pore scale. Therefore, some researchers

have developed models specifically for immiscible displacement at the pore scale. Trantham et al.[47] developed a Stochastic Aggregation Model (SAM) using an improved DLA algorithm to simulate the displacement of groundwater by DNAPLs with both higher and lower viscosities than groundwater. Nsir et al.[48] developed a numerical simulator based on a discrete network model, using pore body and throat size parameters from the particle size distribution of real porous media. The simulated NAPL-water immiscible two-phase flow results matched experimental data.

Cluster 9 (#8 back diffusion): Back diffusion is the process where dissolved DNAPLs migrate into low-permeability zones, accumulate, and then diffuse back into the aquifer after a concentration reversal[49-51]. After source zone DNAPLs are depleted or isolated, back diffusion can occur once the contaminant concentration in the aquifer drops to a certain level, becoming a secondary pollution source and keeping plume concentrations above the MCL over time[4,52]. In recent years, back diffusion has gained attention due to its role in prolonging contamination persistence. Most studies simulate and explore factors influencing its occurrence, such as DNAPL solubility[53,54], soil heterogeneity[49], adsorption-desorption[55,56], and biodegradation[50,57-60]. Simulations of back diffusion are typically divided into two stages, marked by the removal or isolation of the source zone[49,52,61]. In the first stage, contaminants accumulate in low-permeability zones through forward diffusion. In the second stage, after source removal, the simulation continues to study back diffusion by observing plume tailing.

Cluster 10 (#9 contaminant mass discharge): The study of contaminant mass discharge is often closely linked to the mass transfer models in Cluster 3. Considering the challenges and costs of simulating DNAPL dissolution at the field scale, researchers have developed upscaled mass transfer models with domain-averaged coefficients to approximate real-site dissolution processes[34]. Simplified upscaled models, linked to mass discharge flux, can serve as an effective screening tool for evaluating source zone management strategies[36].

In summary, by reviewing and analyzing the current state of research, the distribution of key research hotspots is presented (Figure 6).

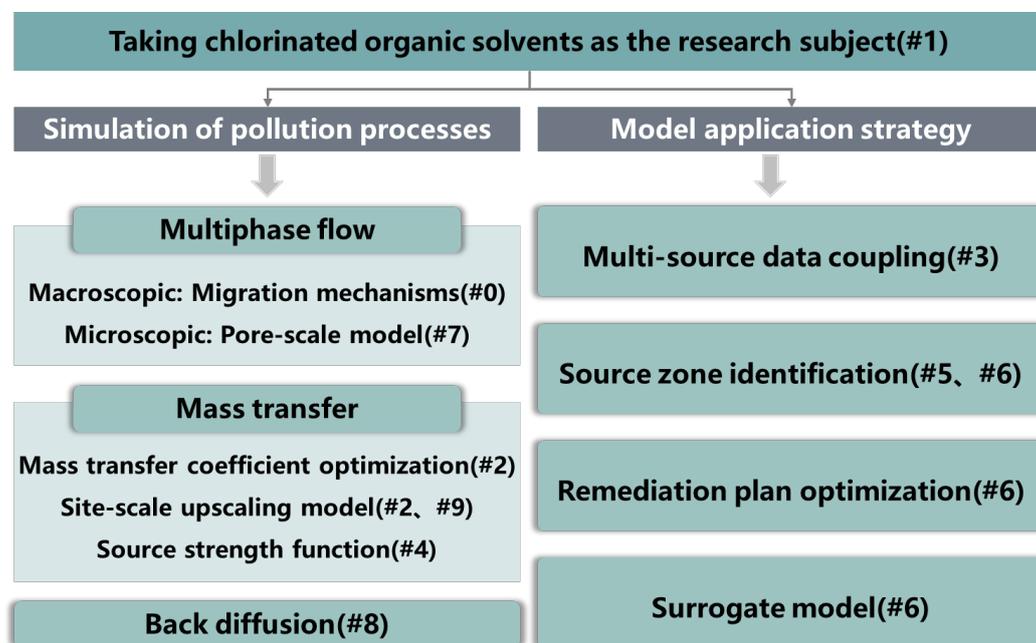


Figure 6. Research hotspots corresponding to the 10 clusters

3.5.2 Assessment of Future Research Trends

The top 20 keywords with the highest burst strength from 1993 to 2023 are identified (Table 3). Based on the analysis of publication volume, the 30-year period can be divided into three stages: the initial budding stage (1993-1999), the rapid development stage (2000-2010), and the continuous breakthrough stage (2011-2023). The main keywords during the initial budding stage were “two-

phase flow”, “multiphase flow”, and “contaminant transport”, with research focusing on the simulation of DNAPL multiphase migration. During the rapid development stage, more detailed descriptions were considered, including shifts in contaminant types (from TCE to PCE), applications in heterogeneous sites, deeper exploration of mass transfer processes, and increased emphasis on NAPL depletion in the source zone. In the continuous breakthrough stage, the focus shifted toward contaminant removal and remediation, the impact of permeability, back diffusion in low-permeability zones, and the integration of geophysical techniques for source zone identification.

From a research trend perspective, DNAPL modeling has developed into a well-established system, with further studies primarily focused on optimizing model details based on experimental findings. Future research directions include: (1) investigating back diffusion mechanisms and exploring methods to reduce plume persistence; (2) applying models to real sites for source zone characterization and pollution distribution; (3) optimizing remediation strategies to enhance effectiveness and reduce costs.

Table 3. Top 20 keywords with the strongest citation bursts.

Keywords	Strength	Begin	End	1993-2023 *
two phase flow	6.09	1998	2004	
multiphase flow	5.05	1998	2005	
contaminant transport	4.93	1998	2003	
nonaqueous phase liquids	4.35	2000	2008	
field	3.65	2002	2009	
TCE	5.89	2003	2007	
behavior	4.67	2004	2009	
heterogeneous porous media	4.55	2004	2014	
source strength functions	5.98	2008	2016	
NAPL dissolution	4.87	2008	2013	
partial mass depletion	4.82	2008	2012	
reductive dechlorination	7.01	2009	2015	
PCE	3.54	2009	2015	
DNAPL	4.22	2014	2020	
back diffusion	5.23	2016	2022	
permeability	4.13	2017	2023	
enhanced aquifer remediation	3.62	2017	2018	
DNAPL migration	3.98	2018	2023	
removal	3.73	2019	2023	
tomography	3.69	2021	2023	

* Red bars show keyword burst periods, dark blue bars indicate post-burst periods, and light blue bars represent pre-appearance periods.

4. Summary and Outlook

This study conducted a bibliometric analysis using CiteSpace on 614 DNAPL modeling-related publications from the WoS core database (1993-2023). The findings are as follows:

(1) DNAPL models remain a focus of scholarly attention, with research outputs continuing to grow steadily. The United States is leading the international research on DNAPL models, followed by China and Canada. However, research priorities vary across countries, and international collaboration and exchange need to be strengthened.

(2) The core of DNAPL model research focuses on the simulation of DNAPL migration, transformation, and pollution distribution. In terms of published journals, the field is highly specialized with limited broader impact. To raise awareness and increase research impact, developing a health risk assessment model based on DNAPL contamination and strengthening cross-disciplinary connections could be beneficial.

(3) Based on keyword clustering analysis, the key research hotspots related to DNAPL models focus on multiphase flow models, mass transfer models, back diffusion, and practical applications of the models.

(4) Based on keyword burst analysis, the research trends in DNAPL modeling are centered on back diffusion mechanisms, characterization of contamination source zones and prediction of contaminant distribution in real-world sites, as well as the optimization of remediation strategies.

Author Contributions: M.J.: conceptualization, formal analysis, visualization, writing original draft; X.L.: conceptualization, visualization, writing original draft; R.W.: conceptualization and visualization; Z.X.: conceptualization, review and editing, supervision; H.Y.: conceptualization, methodology, review and editing, supervision.

Funding: This research was funded by the National Key Research and Development Project (Grant 2020YFC1808201).

Data Availability Statement: Not applicable

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Ajo-Franklin, J.B.; Geller, J.T.; Harris, J.M. A survey of the geophysical properties of chlorinated DNAPLs. *Journal of Applied Geophysics* **2006**, *59*, 177-189, doi:10.1016/j.jappgeo.2005.10.002.
2. Wu, W.J.; Delshad, M.; Oolman, T.; Pope, G.A. Remedial Options for Creosote- Contaminated Sites. *Groundwater Monitoring & Remediation* **2000**, *20*, 78-86, doi:10.1111/j.1745-6592.2000.tb00268.x.
3. Okuda, N.; Shimizu, T.; Muratani, M.; Terada, A.; Hosomi, M. Study of penetration behavior of PCB-DNAPL in a sand layer by a column experiment. *Chemosphere* **2014**, *114*, 59-68, doi:10.1016/j.chemosphere.2014.03.091.
4. Parker, B.L.; Chapman, S.W.; Guilbeault, M.A. Plume persistence caused by back diffusion from thin clay layers in a sand aquifer following TCE source-zone hydraulic isolation. *Journal of Contaminant Hydrology* **2008**, *102*, 86-104, doi:10.1016/j.jconhyd.2008.07.003.
5. Pan, Y.; Zeng, X.; Xu, H.; Sun, Y.; Wang, D.; Wu, J. Assessing human health risk of groundwater DNAPL contamination by quantifying the model structure uncertainty. *Journal of Hydrology* **2020**, *584*, doi:10.1016/j.jhydrol.2020.124690.
6. Schaerlaekens, J.; Carmeliet, J.; Feyen, J. Multi-objective optimization of the setup of a surfactant-enhanced DNAPL remediation. *Environ. Sci. Technol.* **2005**, *39*, 2327-2333.
7. Schaerlaekens, J.; Mertens, J.; Van Linden, J.; Vermeiren, G.; Carmeliet, J.; Feyen, J. A multi-objective optimization framework for surfactant-enhanced remediation of DNAPL contaminations. *Journal of Contaminant Hydrology* **2006**, *86*, 176-194, doi:10.1016/j.jconhyd.2006.03.002.
8. West, M.R.; Kueper, B.H. Numerical simulation of DNAPL source zone remediation with in situ chemical oxidation (ISCO). *Advances in Water Resources* **2012**, *44*, 126-139, doi:10.1016/j.advwatres.2012.05.001.
9. Kim, U.; Parker, J.C.; Borden, R.C. Stochastic cost-optimization and risk assessment of in situ chemical oxidation for dense non-aqueous phase liquid (DNAPL) source remediation. *Stochastic Environmental Research and Risk Assessment* **2019**, *33*, 73-89, doi:10.1007/s00477-018-1633-y.
10. Liu, Y.; Barbara S. Minsker, M.A. Full Multiscale Approach for Optimal Control of In Situ Bioremediation. *Journal of Water Resources Planning and Management* **2004**, *130*, 26-32.
11. Zare, F.; Elsayah, S.; Iwanaga, T.; Jakeman, A.J.; Pierce, S.A. Integrated water assessment and modelling: A bibliometric analysis of trends in the water resource sector. *Journal of Hydrology* **2017**, *552*, 765-778, doi:10.1016/j.jhydrol.2017.07.031.
12. Chen, C. CiteSpace II: Detecting and visualizing emerging trends and transient patterns in scientific literature. *Journal of the American Society for Information Science and Technology* **2005**, *57*, 359-377, doi:10.1002/asi.20317.
13. Guleria, A.; Gupta, P.K.; Chakma, S.; Yadav, B.K. Unraveling the Fate and Transport of DNAPLs in Heterogeneous Aquifer Systems—A Critical Review and Bibliometric Analysis. *Sustainability* **2023**, *15*, doi:10.3390/su15108214.
14. Erning, K.; Grandel, S.; Dahmke, A.; Schäfer, D. Simulation of DNAPL infiltration and spreading behaviour in the saturated zone at varying flow velocities and alternating subsurface geometries. *Environmental Earth Sciences* **2012**, *65*, 1119-1131, doi:10.1007/s12665-011-1361-9.
15. Dekker, T.J.; Abriola, L.M. The influence of field-scale heterogeneity on the infiltration and entrapment of dense nonaqueous phase liquids in saturated formations. *Contaminant Hydrology* **2000**, *42*, 187-218.
16. Lemke, L.D.; Abriola, L.M.; Goovaerts, P. Dense nonaqueous phase liquid (DNAPL) source zone characterization: Influence of hydraulic property correlation on predictions of DNAPL infiltration and entrapment. *Water Resources Research* **2004**, *40*, doi:10.1029/2003wr001980.
17. Cheng, Z.; Lu, G.; Wu, M.; Hao, Y.; Mo, C.; Li, Q.; Wu, J.; Wu, J.; Hu, B.X. The Effects of Spill Pressure on the Migration and Remediation of Dense Non-Aqueous Phase Liquids in Homogeneous and Heterogeneous Aquifers. *Sustainability* **2023**, *15*, doi:10.3390/su151713072.
18. Kueper, B.H.; Redman, D.; Starr, R.C.; Reitsma, S.; Mah, M. A Field Experiment to Study the Behavior of Tetrachloroethylene Below the Water Table: Spatial Distribution of Residual and Pooled DNAPL. *Groundwater* **1993**, *31*, 756-766, doi:10.1111/j.1745-6584.1993.tb00848.x.
19. Bradford, S.A.; Abriola, L.M.; Rathfelder, K.M. Flow and entrapment of dense nonaqueous phase liquids in physically and chemically heterogeneous aquifer formations. *Advances in Water Resources* **1998**, *22*, 117-132.
20. Wu, M.; Yang, Y.; Lin, J.; Wu, J.; Wu, J.; Hu, B.X. The co-effect of heterogeneity and solute concentration on representative elementary volume of DNAPL in groundwater. *Journal of Hydrology* **2020**, *585*, doi:10.1016/j.jhydrol.2020.124795.
21. Gerhard, J.I.; Kueper, B.H. Relative permeability characteristics necessary for simulating DNAPL infiltration, redistribution, and immobilization in saturated porous media. *Water Resources Research* **2003**, *39*, doi:10.1029/2002wr001490.
22. Gerhard, J.I.; Kueper, B.H. Influence of constitutive model parameters on the predicted migration of DNAPL in heterogeneous porous media. *Water Resources Research* **2003**, *39*, doi:10.1029/2002wr001570.

23. Gerhard, J.I.; Kueper, B.H. Capillary pressure characteristics necessary for simulating DNAPL infiltration, redistribution, and immobilization in saturated porous media. *Water Resources Research* **2003**, *39*, doi:10.1029/2002wr001270.
24. Zheng, F.; Gao, Y.; Sun, Y.; Shi, X.; Xu, H.; Wu, J. Influence of flow velocity and spatial heterogeneity on DNAPL migration in porous media: insights from laboratory experiments and numerical modelling. *Hydrogeology Journal* **2015**, *23*, 1703-1718, doi:10.1007/s10040-015-1314-6.
25. Fagerlund, F.; Illangasekare, T.H.; Phenrat, T.; Kim, H.J.; Lowry, G.V. PCE dissolution and simultaneous dechlorination by nanoscale zero-valent iron particles in a DNAPL source zone. *Journal of Contaminant Hydrology* **2012**, *131*, 9-28, doi:10.1016/j.jconhyd.2011.08.011.
26. Pierce, A.A.; Chapman, S.W.; Zimmerman, L.K.; Hurley, J.C.; Aravena, R.; Cherry, J.A.; Parker, B.L. DFN-M field characterization of sandstone for a process-based site conceptual model and numerical simulations of TCE transport with degradation. *Journal of Contaminant Hydrology* **2018**, *212*, 96-114, doi:10.1016/j.jconhyd.2018.03.001.
27. Yang, J.H.; Lee, K.K.; Clement, T.P. Impact of seasonal variations in hydrological stresses and spatial variations in geologic conditions on a TCE plume at an industrial complex in Wonju, Korea. *Hydrological Processes* **2012**, *26*, 317-325, doi:10.1002/hyp.8236.
28. Feo, A.; Pinardi, R.; Artoni, A.; Celico, F. Three-Dimensional High-Precision Numerical Simulations of Free-Product DNAPL Extraction in Potential Emergency Scenarios: A Test Study in a PCE-Contaminated Alluvial Aquifer (Parma, Northern Italy). *Sustainability* **2023**, *15*, doi:10.3390/su15129166.
29. Zhu, J.; Sykes, J.F. The influence of NAPL dissolution characteristics on field-scale contaminant transport in subsurface. *Journal of Contaminant Hydrology* **2000**, *41*, 133-154.
30. Nambi, I.M.; Powers, S.E. Mass transfer correlations for nonaqueous phase liquid dissolution from regions with high initial saturations. *Water Resources Research* **2003**, *39*, doi:10.1029/2001wr000667.
31. Maji, R.; Sudicky, E.A. Influence of mass transfer characteristics for DNAPL source depletion and contaminant flux in a highly characterized glaciofluvial aquifer. *Journal of Contaminant Hydrology* **2008**, *102*, 105-119, doi:10.1016/j.jconhyd.2008.08.005.
32. Luciano, A.; Mancini, G.; Torretta, V.; Viotti, P. An empirical model for the evaluation of the dissolution rate from a DNAPL-contaminated area. *Environmental Science and Pollution Research* **2018**, *25*, 33992-34004, doi:10.1007/s11356-018-3193-6.
33. Parker, J.C.; Park, E. Modeling field-scale dense nonaqueous phase liquid dissolution kinetics in heterogeneous aquifers. *Water Resources Research* **2004**, *40*, doi:10.1029/2003wr002807.
34. Christ, J.A.; Ramsburg, C.A.; Pennell, K.D.; Abriola, L.M. Estimating mass discharge from dense nonaqueous phase liquid source zones using upscaled mass transfer coefficients: An evaluation using multiphase numerical simulations. *Water Resources Research* **2006**, *42*, doi:10.1029/2006wr004886.
35. Saenton, S.; Illangasekare, T.H. Upscaling of mass transfer rate coefficient for the numerical simulation of dense nonaqueous phase liquid dissolution in heterogeneous aquifers. *Water Resources Research* **2007**, *43*, doi:10.1029/2005wr004274.
36. Christ, J.A.; Ramsburg, C.A.; Pennell, K.D.; Abriola, L.M. Predicting DNAPL mass discharge from pool-dominated source zones. *Journal of Contaminant Hydrology* **2010**, *114*, 18-34, doi:10.1016/j.jconhyd.2010.02.005.
37. Kokkinaki, A.; Werth, C.J.; Sleep, B.E. Comparison of upscaled models for multistage mass discharge from DNAPL source zones. *Water Resources Research* **2014**, *50*, 3187-3205, doi:10.1002/2013wr014663.
38. Boroumand, A.; Abriola, L.M. On the upscaling of mass transfer rate expressions for interpretation of source zone partitioning tracer tests. *Water Resources Research* **2015**, *51*, 832-847, doi:10.1002/2014wr015767.
39. Power, C.; Gerhard, J.I.; Tsourlos, P.; Giannopoulos, A. A new coupled model for simulating the mapping of dense nonaqueous phase liquids using electrical resistivity tomography. *Geophysics* **2013**, *78*, EN1-EN15, doi:10.1190/geo2012-0395.1.
40. Kang, X.; Kokkinaki, A.; Kitanidis, P.K.; Shi, X.; Lee, J.; Mo, S.; Wu, J. Hydrogeophysical Characterization of Nonstationary DNAPL Source Zones by Integrating a Convolutional Variational Autoencoder and Ensemble Smoother. *Water Resources Research* **2021**, *57*, doi:10.1029/2020wr028538.
41. Kang, X.; Kokkinaki, A.; Power, C.; Kitanidis, P.K.; Shi, X.; Duan, L.; Liu, T.; Wu, J. Integrating deep learning-based data assimilation and hydrogeophysical data for improved monitoring of DNAPL source zones during remediation. *Journal of Hydrology* **2021**, *601*, doi:10.1016/j.jhydrol.2021.126655.
42. Kang, X.; Power, C.; Kokkinaki, A.; Revil, A.; Wu, J.; Shi, X.; Deng, Y. Characterization of DNAPL source zones in clay-sand media via joint inversion of DC resistivity, induced polarization and borehole data. *Journal of Contaminant Hydrology* **2023**, *258*, doi:10.1016/j.jconhyd.2023.104240.
43. Falta, R.W.; Suresh Rao, P.; Basu, N. Assessing the impacts of partial mass depletion in DNAPL source zones I. Analytical modeling of source strength functions and plume response. *Journal of Contaminant Hydrology* **2005**, *78*, 259-280, doi:10.1016/j.jconhyd.2005.05.010.

44. Wang, Z.; Lu, W.; Chang, Z.; Luo, J. A combined search method based on a deep learning combined surrogate model for groundwater DNAPL contamination source identification. *Journal of Hydrology* **2023**, *616*, doi:10.1016/j.jhydrol.2022.128854.
45. Hou, Z.; Lao, W.; Wang, Y.; Lu, W. Cyclic Feedback Updating Approach and Uncertainty Analysis for the Source Identification of DNAPL-Contaminated Aquifers. *Journal of Water Resources Planning and Management* **2021**, *147*, doi:10.1061/(asce)wr.1943-5452.0001322.
46. Du, J.; Shi, X.; Mo, S.; Kang, X.; Wu, J. Deep learning based optimization under uncertainty for surfactant-enhanced DNAPL remediation in highly heterogeneous aquifers. *Journal of Hydrology* **2022**, *608*, doi:10.1016/j.jhydrol.2022.127639.
47. Trantham, H.; Durnford, D. Stochastic aggregation model (SAM) for DNAPL–water displacement in porous media. *Journal of Contaminant Hydrology* **1999**, *36*, 377-400.
48. Nsir, K.; Schäfer, G.; di Chiara Roupert, R.; Mercury, L. Pore scale modelling of DNAPL migration in a water-saturated porous medium. *Journal of Contaminant Hydrology* **2018**, *215*, 39-50, doi:10.1016/j.jconhyd.2018.07.001.
49. Yang, L.; Wang, X.; Mendoza-Sanchez, I.; Abriola, L.M. Modeling the influence of coupled mass transfer processes on mass flux downgradient of heterogeneous DNAPL source zones. *J Contam Hydrol* **2018**, *211*, 1-14, doi:10.1016/j.jconhyd.2018.02.003.
50. Ding, X.-H.; Feng, S.-J.; Zheng, Q.-T. Forward and back diffusion of reactive contaminants through multi-layer low permeability sediments. *Water Research* **2022**, *222*, doi:10.1016/j.watres.2022.118925.
51. Feng, C.; Liu, F.; Huang, F.; Chen, L.; Bi, E. Dense nonaqueous phase liquids back diffusion controlled by biodegradation and heterogeneous sorption-desorption. *Journal of Cleaner Production* **2023**, *382*, doi:10.1016/j.jclepro.2022.135370.
52. Chapman, S.W.; Parker, B.L. Plume persistence due to aquitard back diffusion following dense nonaqueous phase liquid source removal or isolation. *Water Resources Research* **2005**, *41*, doi:10.1029/2005wr004224.
53. Chapman, S.W.; Parker, B.L.; Sale, T.C.; Doner, L.A. Testing high resolution numerical models for analysis of contaminant storage and release from low permeability zones. *Journal of Contaminant Hydrology* **2012**, *136-137*, 106-116, doi:10.1016/j.jconhyd.2012.04.006.
54. Adamson, D.T.; de Blanc, P.C.; Farhat, S.K.; Newell, C.J. Implications of matrix diffusion on 1,4-dioxane persistence at contaminated groundwater sites. *Science of The Total Environment* **2016**, *562*, 98-107, doi:10.1016/j.scitotenv.2016.03.211.
55. Maghrebi, M.; Jankovic, I.; Allen-King, R.M.; Rabideau, A.J.; Kalinovich, I.; Weissmann, G.S. Impacts of transport mechanisms and plume history on tailing of sorbing plumes in heterogeneous porous formations. *Advances in Water Resources* **2014**, *73*, 123-133, doi:10.1016/j.advwatres.2014.07.007.
56. Maghrebi, M.; Jankovic, I.; Weissmann, G.S.; Matott, L.S.; Allen-King, R.M.; Rabideau, A.J. Contaminant tailing in highly heterogeneous porous formations: Sensitivity on model selection and material properties. *Journal of Hydrology* **2015**, *531*, 149-160, doi:10.1016/j.jhydrol.2015.07.015.
57. Adamson, D.T.; Chapman, S.W.; Farhat, S.K.; Parker, B.L.; deBlanc, P.; Newell, C.J. Characterization and Source History Modeling Using Low-k Zone Profiles at Two Source Areas. *Groundwater Monitoring & Remediation* **2015**, *35*, 52-69, doi:10.1111/gwmr.12090.
58. Wanner, P.; Parker, B.L.; Hunkeler, D. Assessing the effect of chlorinated hydrocarbon degradation in aquitards on plume persistence due to back-diffusion. *Science of The Total Environment* **2018**, *633*, 1602-1612, doi:10.1016/j.scitotenv.2018.03.192.
59. Thouement, H.A.A.; Kuder, T.; Heimovaara, T.J.; van Breukelen, B.M. Do CSIA data from aquifers inform on natural degradation of chlorinated ethenes in aquitards? *Journal of Contaminant Hydrology* **2019**, *226*, doi:10.1016/j.jconhyd.2019.103520.
60. Halloran, L.J.S.; Hunkeler, D. Controls on the persistence of aqueous-phase groundwater contaminants in the presence of reactive back-diffusion. *Science of The Total Environment* **2020**, *722*, doi:10.1016/j.scitotenv.2020.137749.
61. Carey, G.R.; Chapman, S.W.; Parker, B.L.; McGregor, R. Application of an Adapted Version of MT3DMS for Modeling Back-Diffusion Remediation Timeframes. *Remediation Journal* **2015**, *25*, 55-79, doi:10.1002/rem.21440.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.