UNIVERSITY OF CALIFORNIA MERCED

Slipping Through the Cracks: A Geospatial and Treatment Analysis of 1,2,3-Trichloropropane in Drinking Water Supplies

Dissertation submitted in partial satisfaction of the requirements for the degree
Doctor of Philosophy

in

Environmental Systems

by

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2024

Dedication

This work is dedicated to the 2 billion people who lack access to safe drinking water.

Epigraph

"The most alarming of all man's assaults upon the environment is the contamination of air, earth, rivers, and sea with dangerous and even lethal materials. This pollution is for the most part irrecoverable; the chain of evil it initiates not only in the world that must support life but in living tissues is for the most part irreversible. In this now universal contamination of the environment, chemicals are the sinister and little-recognized partners of radiation in changing the very nature of the world — the very nature of its life."

Rachel Carson
Silent Spring, 1962

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List of Abbreviations

Abbreviation	**Definition**
BAT	Best available technology
BRT	Boosted regression trees
CART	Classification and regression trees
EDF	Empirical distribution function
GAC	Granular activated carbon
GIS	Geographic information systems
MCL	Maximum contaminant level
MEL	Manufacturer's Estimated Lifetime
P-POU	Pitcher Point-of-Use
PRISMA	Preferred Reporting Items for Systematic Reviews and Meta-Analyses
RF	Random Forest
SDWA	Safe Drinking Water Act
TCP	1,2,3-trichloropropane
ZVI	Zero valent Iron
ZVZ	Zero valent Zinc

Acknowledgments

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I want to express my sincere thanks to my committee members and professors, Drs. Thomas Harmon, Teamrat Ghezzhei, Sarina Ergas, Marc Buetel, Erin Hestir, Josue Medallin-Azuara, and Gerardo Diaz for their invaluable knowledge and advice. Their diverse perspectives and constructive feedback have significantly enhanced my scientific understanding of the natural world.

In addition, I am incredibly lucky to have two amazing feline friends, Frida and Diego, as my animal companions. They appeared on my doorstep before the COVID-19 pandemic and have been a constant source of comfort, laughter, and warmth. Whether keeping me company during long work hours or snuggling with me on chilly nights, they have been a true blessing. They remind me to take breaks and appreciate the little things (even if that means lying on my keyboard!).

Lastly, I would like to express my deep gratitude to my advisor, Dr. Colleen Naughton. Our countless discussions and problem-solving sessions have been invaluable, and your unwavering belief in me has been a driving force behind my success. I could not have done this without your mentorship.

Curriculum Vitae

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OBJECTIVES

Environmental scientist seeking a challenging position to contribute my skills. With more than a decade of experience teaching science in public schools, two years of international development work with the US Peace Corps, and a PhD in Environmental Systems, I am well-equipped to tackle various complex challenges.

EDUCATION

Doctor of Philosophy (Ph.D.) Environmental Systems
University of California, Merced, 2024
Relevant coursework: Sustainable Development, Contaminant Mass Transfer, Environmental Modelling and Data Analysis, Antiracism in Environmental Systems, Ecosystem Climate Solutions, Natural Treatment Systems.
Dissertation: *Slipping Through the Cracks: A Geospatial and Treatment Analysis of 1,2,3-TCP in Drinking Water Supplies*

Master of Science (M.S.) Instructional Science and Technology
California State University, Monterey, 2016
Thesis: Chemistry Education Through Inquiry (CETI)

Teaching Credential
University of California, Davis, 2000

Bachelor of Science (B.S.) Microbiology and Molecular Genetics
University of California, Los Angeles, 1997

Advanced Coursework in Genetics
University of London, England, 1994

TECHNICAL AND LANGUAGE SKILLS

ArcGIS, QGIS, R, Adobe Captivate, Microsoft Office
English - Native Speaker
Spanish – Beginner
Kiswahili - Beginner

CERTIFICATIONS

UC Merced 2023	Lab and fire safety training
UC Merced 2020	Institutional Review Board (IRB) Certification for social research
Namaste Yoga 2019	Yoga Teacher Training Certification (RYS-200)

RELEVANT EXPERIENCE

Ph.D. Candidate, Environmental Systems University of California, Merced
Merced, CA, 2019-Present

- Researched with the prestigious FEWS-US lab, actively contributing to the development of sustainable and culturally sensitive Food-Energy-Water systems designed to address critical needs in underserved communities both domestically and internationally
- Authored and co-published a comprehensive body of work, including a hybrid GIS machine-learning model, and a policy paper focused on maximum limits for 1,2,3-TCP, a persistent carcinogen in drinking water
- Taught Environment in Crisis lab section, an engineering course with 80 students
- Created comprehensive lecture materials and lab protocols encompassing a range of crucial subjects, such as disease transmission, pollution, water quality testing, and data analysis
- Coordinated a pioneering summer program that afforded students the unique opportunity to engage in cutting-edge research in agricultural technology
- Provided dedicated mentorship to two undergraduate students, equipping them with valuable research techniques, advanced data analysis skills, and effective scientific communication methods

Science Teacher Acalanes Union High School District
Lafayette, CA, 2006-2019

- Taught dynamic AP Environmental Science and Chemistry classes to high-achievers
- Mentored science clubs and guided professional internships
- Created project-based lessons to engage students in real-world challenges
- Utilized interactive technology for effective teaching and grading
- Employed inquiry-based constructivist learning with technology integration
- Responded professionally to inquiries and maintained accurate records
- Actively attended diversity, tech, and best practice conferences
- Served as a district coach for Next Generation Science Standards training

Science Teacher St. Helena Unified School District
St. Helena, CA, 2004-2006

- Instructed Chemistry, Biology, and Environmental Science classes, and mentored the Science club
- Designed engaging courses stressing measurement, data analysis, and theory
- Applied innovative techniques for teaching science to English language learners

Editorial Assistant, Proceedings of the National Academy of Sciences
Washington D.C., 2002-2004

- Managed manuscript submissions for PNAS, a renowned scientific journal
- Coordinated the peer review process ensuring smooth and efficient operations
- Facilitated effective communication among researchers, publishing personnel, and Academy members
- Wrote comprehensive biographical summaries for esteemed Academy Members

U.S. Peace Corps, Secondary School Science Teacher
Sitatunga, Kenya, 1999 – 2002

- Adapted hands-on techniques to a rural school resulting in increased engagement
- Worked with Greenbelt planting indigenous trees near Saiwa Swamp National Park
- Established an HIV/AIDS Peer Education Group to train students and teachers
- Chaired the Women's Development Group, led national meetings, and earned a U.S. Ambassador award
- Executed an event with over 100 participants to connect rural girls with professional women mentors
- Co-instructed and developed objectives for incoming volunteers on cross-culture, medical, and security

Associate Scientist, Perkin-Elmer Applied Biosystems
Foster City, CA, 1997- 1998

- Sequenced a portion of the X-chromosome for the Human Genome Project
- Analyzed DNA sequences using UNIX and statistical analysis
- Designed a laboratory procedural guide resulting in increased productivity
- Collaborated with coworkers to optimize experimental protocols
- Trained new employees in sequencing chemistry and software applications

PEER-REVIEWED JOURNAL ARTICLES

[1] Hauptman, B. H., Naughton, C. C., Harmon, T.C. (2023). Using Machine Learning to Predict 1,2,3-Trichloropropane Contamination from Legacy Non-point Source Pollution of Groundwater in California's Central Valley. *Groundwater for Sustainable Development.* https://doi.org/10.1016/j.gsd.2023.100955

[2] Hauptman, B. H., & Naughton, C. C. (2021). Unsafe at Low Levels: Adopt a Federal MCL for 1,2,3-Trichloropropane in United States' Drinking Water. *Journal of Science Policy & Governance.* https://doi.org/10.38126/JSPG190104

[3] Hauptman, B. H., & Naughton, C. C. (2021). Legacy 1,2,3-Trichloropropane Contamination: A Systematic Review of Treatments. *Journal of Water, Sanitation and Hygiene for Development.* https://doi.org/10.2166/washdev.2021.006

CONFERENCE PRESENTATIONS (*asterisk indicates presenter)

[1] * Hauptman, B. H., Harmon, T.C., Nasef, Z., Rosales, A.A., Naughton, C. C. *Using point-of-use filters and almond biochar to reduce 1,2,3-TCP contamination in drinking water* [Poster]. University of North Carolina (UNC) Water and Health Conference, 2023.

[2] *Hauptman, B. H., Naughton C.C. *Groundwater Quality and Environmental Justice in Rural Communities* [Panel discussion]. UC ANR Statewide Conference, 2023.

[3] *Hauptman, B. H., Naughton C.C., Harmon, T.C. *Using Machine Learning to Predict 1,2,3-Trichloropropane Contamination from Legacy Non-point Source Pollution of Groundwater in California's Central Valley* [Poster]. ARCS Symposium, 2023.

[4] *Hauptman, B. H., Naughton C.C., Deubel T., Bargach, J., Amayous N., Hernandez A., *Impacts of Urban Expansion into Argan Forests in Morocco* [Panel]. Society for Applied Anthropology Annual Meeting, 2023.

[5] *Hauptman, H. B., Naughton C.C., *Using Random Forest to Predict Groundwater Contaminated with 1,2,3-TCP in California's Central Valley* [Online panel]. American Geophysical Union (AGU) Annual Meeting, 2021.

[6] *Hauptman, H. B., Naughton C.C., *A Geospatial Analysis of 1,2,3-Trichloropropane (TCP) in the San Joaquin Valley,* [Online panel]. California Department of Food and Agriculture, PUR Annual Meeting, 2021.

[7] *Hauptman, H. B., Naughton C.C., *Merced Community Food Map Dashboard* [Online presentation]. Merced County GIS User Group, 2021. (http://bit.ly/MercedFoodMap)

[8] *Hauptman, B. H., Naughton C.C., *A Toxic Inheritance: Legacy 1,2,3-Trichloropropane in Groundwater - A Systematic Review of Treatments* [Poster]. University of North Carolina (UNC) Water and Health Conference, 2020.

[9] *Hauptman, B. H., Naughton C.C., *Legacy Contaminant Removal: 1,2,3-Trichloropropane Treatment Methods – A Systematic Review* [Poster]. UC Merced Research Showcase, 2020

VOLUNTEER EXPERIENCE

Pop-Up People's Pantry and People's Garden Volunteer, Merced, CA, 2021-2023

- Served fresh, free food to the community, reducing food waste and food insecurity
- Created a bilingual GIS Dashboard locating affordable produce in Merced

Davis Community Homeless Shelter Volunteer, Davis, CA, 1998-1999

- Managed shelter and intake in the evenings and overnight two days per week
- Registered residents while managing social opportunities, medication, and pantry

AFFILIATIONS

The Society for Applied Anthropology – 2022 to Present
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National Science Teachers Association – 2003 to 2018

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Achievement Rewards for College Scientists Foundation Scholarship Award – 2022
Rotary Fellowship Award – 2022
Environmental Systems Bobcat Summer Fellowship Award – 2021
Environmental Systems Bobcat Summer Fellowship Award – 2020
U.S. Ambassador Service Excellence Honor– 2003

Slipping Through the Cracks: A Geospatial and Treatment Analysis of 1,2,3-Trichloropropane in Drinking Water Supplies

by B. Hope Hauptman
Doctor of Philosophy in Environmental Systems
University of California, Merced, 2023
Professor Colleen C. Naughton, advisor

Dissertation Abstract

Between the 1940s and the 1980s, 1,2,3-trichloropropane (TCP) was widely applied to agricultural soils as an impurity in soil fumigants to eliminate plant parasitic nematodes. TCP is a suspected human carcinogen that has subsequently leached into groundwater, contaminating numerous wells across North America, Europe, and Asia. In this dissertation, I investigated TCP contamination in groundwater through geospatial mapping and treatment analysis. First, I conducted a systematic review of available treatment technologies in peer-reviewed literature. I found that granular activated carbon (GAC), bioremediation, and chemical reduction using Zero Valent Zinc (ZVZ) are the most effective methods for reducing TCP levels in groundwater. However, the practicality of GAC technology is hindered by its low to moderate adsorption capacity which necessitates frequent media replacement. I also found that the global prevalence of TCP contamination in the hydrosphere needs increased monitoring and modeling. To address the dearth of monitoring data, I developed a predictive model for TCP contamination in California's Central Valley, one of America's most important agricultural regions. I used three decision tree machine-learning models to predict TCP contamination in groundwater using various explanatory variables. The Random Forest algorithm emerged as the top performer, with precipitation, redox state, and nitrate levels as the most important predictive variables. To estimate the scale of contamination in California, I performed a mass balance model to estimate that between 110,000 to 4.3 million kg of TCP have accumulated in the California subsurface due to historical fumigant applications. Next, I addressed the scarcity of data on point-of-use treatments and alternative carbon feedstocks for TCP removal. I found through lab experiments that pitcher point-of-use filters can reduce TCP levels by up to 99%. Thus, households can use these low-cost filters to reduce the risk of TCP exposure and improve the safety of their water supply. Regarding alternative carbon feedstocks, I performed a batch isotherm analysis of almond biochar. Almond biochar was less efficient compared to coconut shells and coal-based granular activated carbon sorbents. However, considering the lower energy costs of producing almond biochar and its abundance as a local agricultural byproduct, I recommend a Life Cycle Assessment to evaluate its sustainability. Finally, my dissertation concludes with a science policy analysis that recommends a federal maximum contaminant level for TCP for public health. In summary, my investigations yielded valuable results to guide TCP monitoring and treatment efforts and provide practical information and policy guidance to affected communities and decision-makers.

Chapter 1. Introduction

1.1 Environmental systems

To tackle complex environmental challenges, it is necessary to adopt an approach that considers finite resources, waste sinks, overall structures, patterns, cycles, and interdependencies. Approaching the problems piecemeal, trying to solve the problems individually using a partial solutions approach, has proven inefficient and ineffective (Ballew et al., 2019). To increase efficiency and to improve effectiveness requires a systems approach, one that views the problems holistically. A key example of this is ensuring continued access to safe and sustainable drinking water sources as demand increases and surface water sources become less reliable. Achieving this requires the use of tools from a range of disciplines, including engineering, public health, toxicology, computer science, geography, and public policy, to assess causal relationships, address existing problems, and plan for future generations. According to the United Nations, around 2 billion people, or a quarter of the world's population, did not have access to safe drinking water in their homes in 2020, and this number is expected to increase (UN, 2023; Cullmann et al., 2021). As reliance on groundwater for drinking water grows, it is crucial to adopt an environmental systems approach to understand and address chemical contaminants like 1,2,3-trichloropropane (TCP) in groundwater supplies.

This dissertation adopts an environmental approach to enhance the understanding of TCP in groundwater supplies by providing a treatment and geospatial analysis. Chapter 2 reviews the current body of knowledge on TCP removal using an interdisciplinary and systematic approach more frequently used in biological and medical sciences (Moher et al., 2009), which offers a less biased and more comprehensive survey of existing research. Chapter 3 addresses the lack of TCP monitoring data and distribution maps using a mass balance and a hybrid machine learning and geospatial approach from computer science, statistics, and environmental engineering fields. Chapter 4 addresses the immediate concerns of households impacted by TCP contamination without treatment facilities by testing affordable point-of-use household and almond biochar treatments to reduce TCP levels in drinking water. Chapter 5 provides a state and federal policy overview, examines public health and toxicology research, defines stakeholders, and offers future science policy considerations.

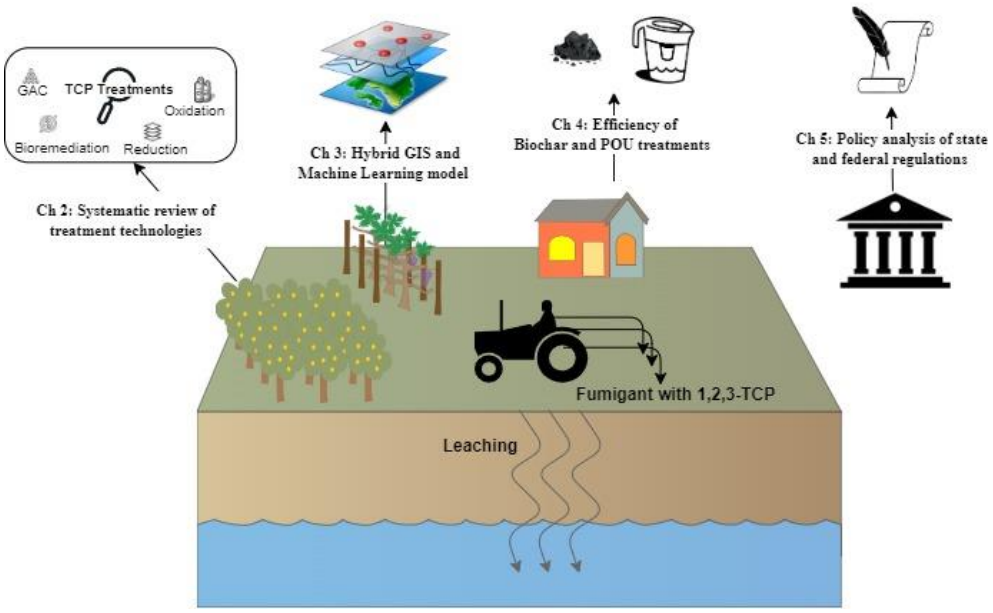

Figure 1 Dissertation overview. Made with online diagram software draw.io

1.2 Groundwater as drinking water

Globally approximately one-third of freshwater is underground and supplies about half of the world's drinking water (Smith et al., 2018). In the future, changing hydrologic extremes due to climate change have the potential to intensify the world's reliance on groundwater as use tends to increase during drought periods when surface water sources are limited (Ravenscroft et al., 2022). Disturbances caused by over-pumping and subsequent subsidence of groundwater aquifers may also transport pollutants into previously uncontaminated wells within the aquifer (Levy et al., 2021).

Groundwater quality depends on many factors and contamination can be influenced by geogenic causes such as excess manganese and fluoride as well as anthropogenic additions of nitrate and/or pesticides (Lapworth et al., 2022). Shallower domestic (a.k.a. private) wells can have higher contaminant concentrations as they often draw water from shallow, unconfined aquifers that are susceptible to pollution from human activities on the land surface (Burow et al., 2019). A USGS study shows that domestic wells have a higher mean concentration of TCP than found in deeper public supply wells (Burow et al., 2019).

Transitioning to the semi-arid Central Valley of California, where groundwater serves as the primary source for 95% of the drinking water, sheds light on the specific challenges faced by its residents. Approximately half a million individuals depend on unregulated groundwater from domestic wells for their water needs (MacLeod and Méndez-Barrientos, 2019; Pauloo et al., 2020). The absence of regulatory oversight in these systems significantly elevates the risks of contaminant exposure for domestic well users compared to those reliant on community water systems (Pace et al., 2019). Compounding this issue, research indicates that a disproportionate number of communities in California relying on domestic wells face disadvantages and financial barriers to monitoring and treating their well water (Pace et al., 2019; London et al., 2021).

1.3 TCP Background

1.3.1 History of use

The presence of anthropogenic contaminants can be classified into two main categories: point source and non-point source (Loague, 2006). Point source refers to contaminants that have identifiable sources, such as a chemical spill, while non-point source contaminants come from diffuse sources, like the runoff of pesticides from agricultural areas. TCP contamination falls under both point and non-point categories because it has both industrial and agricultural inputs (Burow et al., 2019).

Before the 1980s, TCP was used as an industrial cleaning and degreasing agent. Today, TCP is produced as a chemical intermediate for other chlorinated compounds and as a polymer cross-linking agent (Merrill et al., 2019). TCP is also formed as a byproduct in the synthesis of epichlorohydrin, which is used in coatings, adhesives, and plastics (Kim et al., 2023). The US Environmental Protection Agency (EPA) Toxic Release Inventory (TRI) program reports that between 2012-2021 62,344 pounds of TCP were released into the environment from industrial facilities in Texas, Louisiana, South Carolina, and Ohio, with 44% released to land, 23% released to water, and 33% released to the air (EPA, 2021) (Figure 2). The EPA notes that "releases" can include activities such as “spilling, leaking, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing into the environment.”

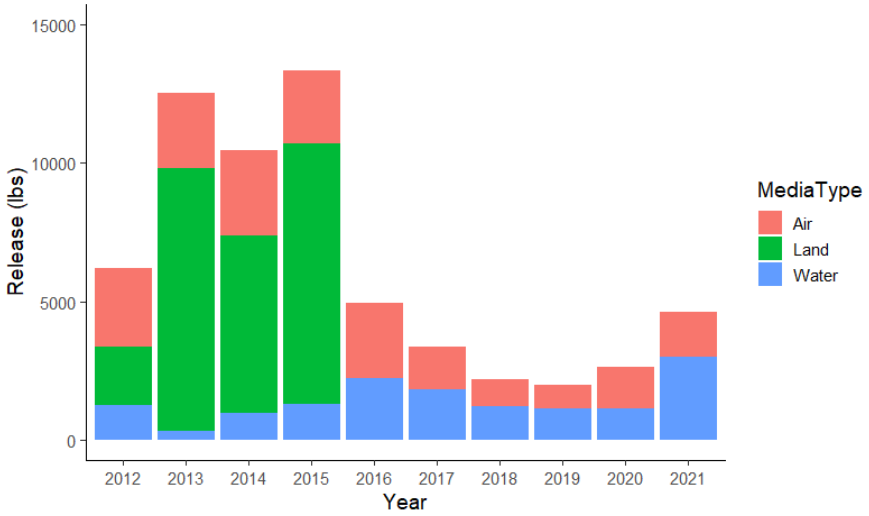

Figure 2 1,2,3-Trichloropropane environmental releases (lbs) by year in the United States. Data from the USEPA toxics tracker.

TCP’s non-point source entry into groundwater is due to the application of TCP-containing pesticides (Burow et al., 2019). Prior to 1985, TCP was produced as an unintended impurity (0.17-7% by mass) in the production of dichloropropene-based fumigants, such as Telone and D-D mix, that were used to kill nematodes in the soil (Oki and Giambelluca, 1987; Zebarth et al., 1998). These fumigants were used to cultivate a wide range of crops, including grapes, citrus and orchard fruits, pineapples, soybeans, cotton, tomatoes, potatoes, and row crops (CDFA, 1970-1984). In chapter 3 of this dissertation, I present a mass balance of TCP contamination in California and estimate the amount of TCP that leached into groundwater from legacy agricultural use.

1.3.2 Physicochemical properties and environmental fate and transport

TCP falls under the category of Volatile Organic Contaminants (VOCs) but stands out due to its low vapor pressure and relatively high boiling point compared to other VOCs like Trichloroethylene (TCE) and Tetrachloroethylene (PCE) (Merrill, 2019). Despite this, it can still leach from soil due to its moderate solubility and low organic carbon partitioning coefficient. In groundwater, TCP concentrations range from low nanograms per liter (ng/L) to micrograms per liter (μg/L), while in soil, they range from micrograms per kilogram (μg/kg) to milligrams per kilogram (mg/kg) (Merrill et al., 2021). Volatilization and leaching to groundwater are the main mechanisms of loss in unsaturated soil (Merrill et al., 2021).

Once TCP is in the atmosphere, it is believed to photodegrade with a half-life of 15 to 46 days (USEPA, 2017). Although under basic conditions TCP is readily hydrolyzed, TCP is relatively resistant to natural biotic and abiotic degradation in circumneutral groundwater, with half-lives in the hundreds of years according to literature (Hauptman and Naughton, 2021). Both aerobic and anaerobic degradation of TCP has been shown in the research (Samin & Janssen, 2012). TCP can degrade cometabolically in the presence of methane or propane-oxidizing bacteria. Anaerobic degradation may occur via reductive dichlorination, generating DCP. Additionally, TCP may degrade via dihaloelimination and reductive dichlorination resulting in propene end products. (Hauptman and Naughton, 2021)

1.3.3 Distribution

TCP has been detected in groundwater in three continents: North America, Europe, and Asia. There is no available information in the literature about the rest of the world but contamination is likely (Chapter 2). In the United States TCP has been found in the groundwater of 13 states and Puerto Rico (Chapter 5). California is the most impacted state with 6.5% of 1,237 wells sampled by the U. S. Geological Survey (USGS) in 2017 detecting TCP at or above the 5 ppt California state maximum contaminant level. A higher percentage of TCP detections in California are in domestic wells (8%) compared to public-supply wells (5%) (Burow et al., 2019).

1.3.4 Health effects

1,2,3-Trichloropropane is strongly predicted to be a human carcinogen based on evidence of carcinogenicity in animal models. In rats and mice, ingesting TCP has been shown to significantly increase the probability of developing malignant tumors in multiple organs (WHO, 2011). Anticipated carcinogenic health effects in humans have led to multiple U.S. states establishing maximum contaminant levels (MCLs) in drinking water. Hawaii, New Jersey, and California have set MCLs of 600, 30, and 5 ppt respectively (Hauptman and Naughton, 2021). As of 2023, there is no federal policy to regulate TCP in drinking water (Chapter 5).

1.4 Chapter 1 References

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Chapter 2. Legacy 1,2,3-Trichloropropane Contamination: A Systematic Review of Treatments[(A)]

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Abstract

1,2,3-Trichloropropane (TCP), a suspected human carcinogen, is a widespread contaminant that leaches into groundwater, where it persists. This systematic review of studies examines treatment technologies for TCP contamination. A four-database search yielded 1,160 papers, 36 of which met the eligibility criteria for a full-text review. The three most-represented treatment technologies, such as biodegradation (13), zerovalent transition metals (8), and granular activated carbon (GAC) (4), are either fully deployed in water systems or in the field test stage. To meet TCP treatment goals, additional site-specific testing of well water is needed since source water chemistry and co-contamination influence treatment efficacy. Future studies should include standardized units for reporting degradation or sorption normalized to surface area, chemical input, and/or energy expenditures. Although GAC is the most common treatment for contaminated wells, this technology remains limited due to a low TCP adsorption capacity which requires frequent bed-volume replacement. Aerobic biodegradation, reduction with zerovalent iron, and Fenton's treatment produce byproducts that could limit their use. A geospatial analysis of TCP treatment studies reveals a dearth of knowledge about the extent of TCP contamination. TCP contamination is documented in at least nine countries on three continents, but there is little information about the rest of the world.

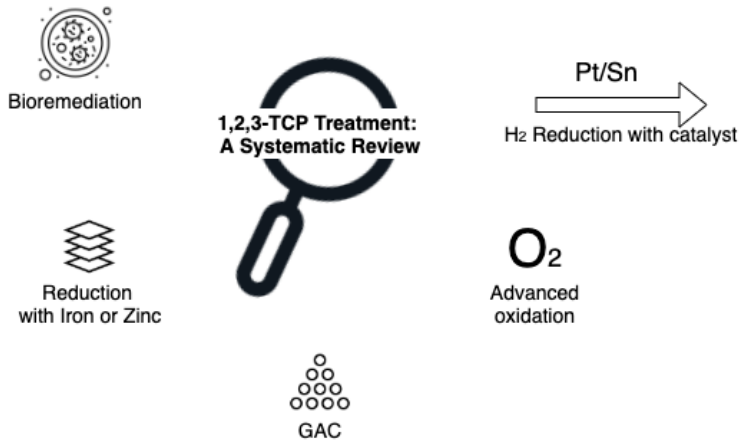

Figure 3 Graphical abstract

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Key words
1,2,3-TCP, granulated activated carbon (GAC), groundwater treatment, legacy contaminant, United Nations Sustainable Development Goal 3 and 6

Highlights

- First systematic review of 1,2,3-trichloropropane (TCP) treatment studies.
- The most highly developed technologies are GAC, zerovalent zinc, and bioremediation.
- Source water chemistry and co-contamination influence TCP treatment efficacy.
- Studies need standardized TCP removal reporting units normalized to the surface area.
- TCP contamination studied in only three continents, revealing wide knowledge gaps.

2.1 Introduction

Thousands of new substances are added to the Chemical Abstract Service (CAS) registry each day. In 2019 CAS registered its 150 millionth unique substance, 50 million of which were catalogued in the last four years alone (Wang, 2019). While the manufacture and utilization of new chemical compounds produced is increasing globally, the environmental fate and effects of many of these chemicals are unknown. People living in Low- and Middle-Income countries (LMICs) may be even more vulnerable to an increase in production. Chemical manufacturing companies, attracted by low labor costs and lax or absent chemical use and disposal regulations, are increasingly moving their operations to LMICs (Kearns et al., 2019).

As new chemicals are produced and disposed of without consideration for their ultimate fate in the environment, the chances increase that some of these chemicals will cause serious problems for global water quality and public health (Damania et al., 2019). Moreover, water and wastewater treatment plants are not always designed to treat these pollutants, and many will have to take a more costly and reactive "end of pipe" approach to treatment (Alpizar et al., 2019; Mohapatra and Kirpalani, 2019). Some of these chemical compounds are recalcitrant, degrading slowly and persisting for long periods, threatening drinking water sources long after their use (Reemtsma et al., 2016). An example is 1,2,3-trichloropropane (TCP), a man-made legacy pollutant banned from use in the United States (U.S.) in 1984, but found in groundwater today (Burow et al., 2019). TCP is a persistent chlorinated hydrocarbon that was previously present in soil fumigants sold under the trade names Telone and D-D as well as an industrial solvent and degreaser. A dense liquid with a low soil organic carbon-water partition coefficient, TCP does not readily sorb to soil. When applied, TCP either evaporates or, because of its high soil mobility, leaches into groundwater (US EPA, 2017), where it persists due to long half-life—estimated at 44-77 years—and low biodegradability (Cheremisinoff et al., 2011).

TCP contamination is widespread and detected in groundwater in North America, Europe, and Asia (Kielhorn et al., 2003). In 2011, the European Chemicals Agency put TCP on its Candidate List as a substance of very high concern (SVHC) because it is carcinogenic and toxic to reproduction (ECHA, 2011). Although there is no U.S. federal Maximum Contaminant Level (MCL), the allowable amount of a contaminant in drinking water delivered to consumers, TCP was listed on the U.S. Environmental Protection Agency (EPA)'s Contaminant Candidate List 3 (CCL 3) in 2009 (US EPA, 2009). Some states including California, Hawaii, and New Jersey have set MCLs for TCP at 5 ng/L,

600 ng/L and 30 ng/L respectively (Torralba-Sanchez et al., 2020; U.S. EPA, 2017). California's State Water Resources Control Board (SWRCB) demands that out-of-compliance well operators treat water with an approved method, such as Granulated Activated Carbon (GAC); discontinue well use; drill another well; purchase water; consolidate with other water systems; and/or dilute contaminated water to concentrations below the MCL (SWRCB, 2018).

TCP can also be categorized as a "contaminant of emerging concern," a legacy chemical with newly understood environmental and/or public health consequences (Sauve and Desrosiers, 2014). The California State Water Board says acute exposure to TCP can burn the skin and eyes and that breathing TCP can irritate the throat and lungs and affect concentration, memory, and muscle coordination. Long-term exposure in drinking water may damage the liver and kidneys and increase the likelihood of tumors in multiple organs (US EPA, 2017). TCP ingestion has been shown to cause cancer in animals and is believed to be a cancer risk for humans (WHO, 2011; SWRCB, 2018)

As of 2019 there has not been a systematic review of TCP groundwater treatment studies. Two earlier reviews of TCP treatment options were not systematic (Merrill et al., 2019; Samin and Janssen, 2012). Uncertainty remains about how to proceed in the face of expensive monitoring and removal of TCP from public and private wells. The primary goal of this study is to determine the most effective TCP treatment method through a systematic review of the peer-reviewed research. To achieve this goal, this review will: (1) identify which groundwater treatments are being researched for TCP (both field and bench studies); (2) determine how contaminate reduction varies among treatment types; (3) determine chemical byproducts of the different treatments; (4) map research locations and TCP contamination sites; and (5) identify opportunities for future research.

2.2 Methods

This systematic review follows the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) guidelines for systematic reviews (Moher et al., 2009). Included in this review are published non-systematic reviews and research on TCP with special attention to treatment and/or remediation of contaminated water sources. An initial search exposed a variety of studies ranging from the carcinogenic potential and toxicology of TCP to its use as a precursor to epichlorohydrin manufacture (van Leeuwen et al., 2012). Four online databases were consulted for this review: Science Direct, Web of Science, PubMed, and Engineering Village. Publication date was not considered as an exclusion factor.

From the total number of results in an initial search, papers were transferred to the citation manager, RefWorks, and de-duplicated manually by two reviewers. To confirm results, reviewers manually deleted duplicates after sorting by title, and once again after sorting by author. Although the automatic de-duplicating function within RefWorks has been found to yield the smallest number of false positives (duplicate citations deleted in error) when compared to Mendeley and Endnote deduplication functions, manual de-duplication produces the fewest deduplication errors (Kwon et al., 2015). After duplicates were removed, two reviewers screened the remaining abstracts, keywords, and titles for the presence of "1,2,3-trichloropropane" and direct reference to any variety of treatment to remove TCP from contaminated water. Research papers were included whether the

treatment technology studied was in early bench scale experimental stages or in full-scale use by water utilities.

Finally, the first author independently read the 36 full-length unique studies and classified each by treatment method, percent of contaminate reduction or removal rate, and location of each paper's primary author. Additional results, identified through the references of selected papers, were added if they met the eligibility requirements above.

2.3 Results and discussion

Using 1,2,3-trichloropropane as the single search term in each database produced a total of 1,160 results (Figure 4); and four papers identified in references found in the other eligible papers were also included. All duplicates, a total of 199, were removed. The remaining 965 articles were screened using abstracts and titles, leaving 40 articles that meet the eligibility requirements (inclusion of 1,2,3-trichloropropane and one or more treatment technology). Four papers were excluded because their full text was unavailable (supplementary information Table S11). Overall, this study includes full-text reviews of 36 papers (Table 1).

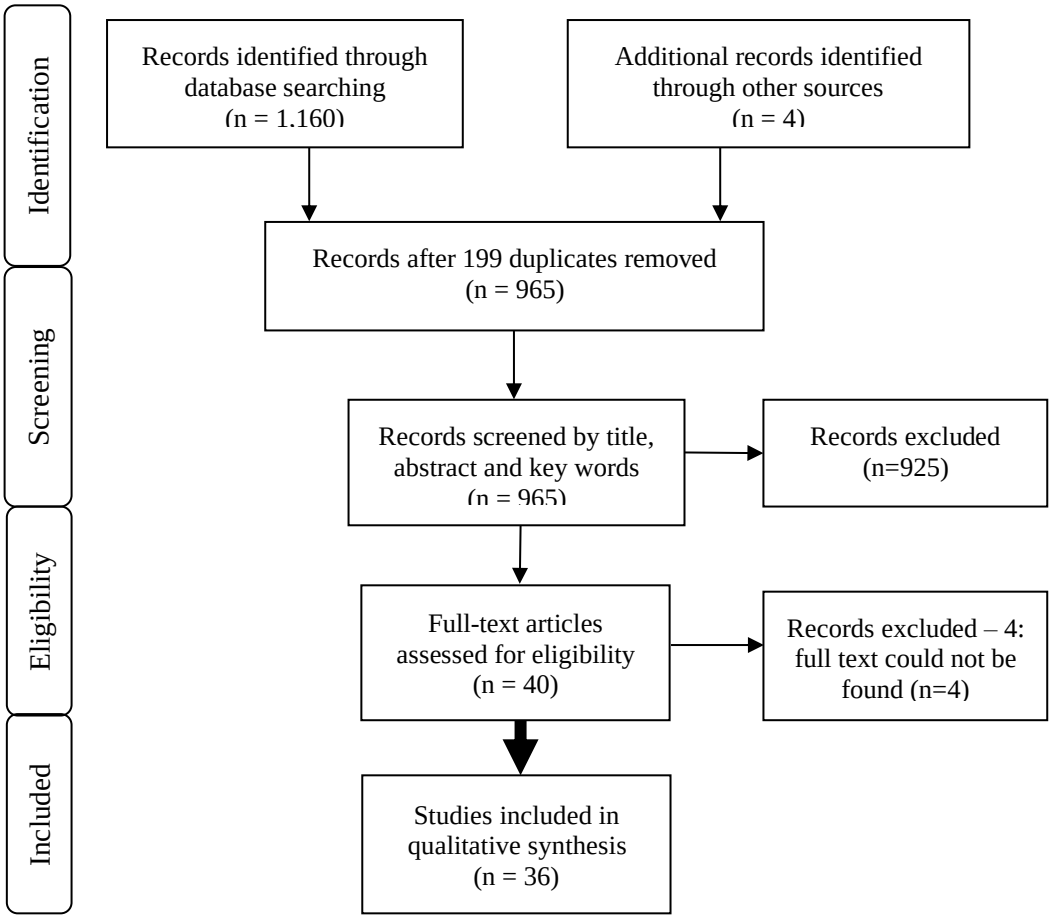

Figure 4 PRISMA flowchart for systematic reviews showing literature search and screening process for 1,2,3-trichloropropane treatment research. Adapted from Moher et al. (2009). Search conducted 09/6/2020

Table 1 Studies included in systematic review of treatment methods for 1,2,3-Tricholoropropane

#	Author (Year)	Title	Type
1	Vannelli et al. (1990)	Degradation of Halogenated Aliphatic Compounds by the Ammonia-Oxidizing Bacterium Nitrosomonas europaea	Bioremediation
2	Hunter (1997)	Fenton's treatment of 1,2,3-trichloropropane: Chemical reaction byproducts, pathway, and kinetics	Fenton reaction
3	Bosma et al. (1998)	Conversion of chlorinated propanes by Methylosinus trichosporium OB3b expressing soluble methane monooxygenase	Bioremediation
4	Bosma et al. (1999)	Utilization of trihalogenated propanes by Agrobacterium radiobacter AD1 through heterologous expression of the haloalkane dehalogenase from Rhodococcus sp. strain M15-3.	Bioremediation
5	Early et al. (2000)	Hydrogen-assisted 1,2,3-trichloropropane dechlorination on supported Pt-Sn catalysts	Hydrogen assisted dechlorination
6	Bosma et al. (2002)	Biodegradation of 1,2,3-trichloropropane through Directed Evolution and Heterologous Expression of a Haloalkane Dehalogenase Gene	Bioremediation
7	Klausen et al. (2003)	Longevity of granular iron in groundwater treatment processes: Solution composition effects on reduction of organohalides and nitroaromatic compounds	ZVI
8	Huang et al. (2005)	Degradation of volatile organic compounds with thermally activated persulfate oxidation	Persulfate
9	Lim et al. (2007)	Sonolysis of chlorinated compounds in aqueous solution	Sonolysis
10	Monincová et al. (2007)	Weak activity of haloalkane dehalogenase LinB with 1,2,3-trichloropropane revealed by X-Ray crystallography and microcalorimetry	Bioremediation
11	*Tratnyek et al. (2008)	Fate and remediation of 1, 2, 3-trichloropropane.	Review
12	Khan et al. (2009)	Effects of iron type in Fenton reaction on mineralization and biodegradability enhancement of hazardous organic compounds	Fenton reaction
13	Pavlova et al. (2009)	Redesigning dehalogenase access tunnels as a strategy for degrading an anthropogenic substrate	Bioremediation
14	Yan et al. (2009)	Isolation of novel bacteria within the Chloroflexi capable of reductive dechlorination of 1,2,3-trichloropropane	Bioremediation
15	Sarathy et al. (2010)	Degradation of 1,2,3-trichloropropane (TCP): Hydrolysis, elimination, and reduction by iron and zinc	ZVI, ZVZ
16	*Tratnyek,et al. (2010b)	Prospects for Remediation of 1, 2, 3-Trichloropropane by Natural and Engineered Abiotic Degradation Reactions.	ZVI, ZVZ, Persulfate
17	Salter-Blanc et al. (2012)	Evaluation of Zerovalent Zinc for Treatment of 1,2,3-trichloropropane-Contaminated Groundwater: Laboratory and Field Assessment	ZVZ
18	Salter-Blanc and Tratnyek (2011)	Effects of solution chemistry on the dechlorination of 1,2,3- trichloropropane by zero-valent zinc	ZVZ
19	Samin and Janssen (2012)	Transformation and biodegradation of 1,2,3-trichloropropane (TCP)	Bioremediation

20	*Harada, 2014	Comparative evaluation of six different granular activated carbon for TCP removal using rapid small-scale column test	GAC
21	Kurumbang et al. (2014)	Computer-Assisted Engineering of the Synthetic Pathway for Biodegradation of a Toxic Persistent Pollutant	Bioremediation
22	Li and Shao (2014)	Biochemical characterization of a haloalkane dehalogenase DadB from Alcanivorax dieselolei B-5.	Bioremediation
23	*Mital, J. (2014)	Granular Activated Carbon Treatment of 1, 2, 3-Trichloropropane	GAC
24	Samin et al. (2014)	A Pseudomonas putida strain genetically engineered for 1,2,3-trichloropropane bioremediation	Bioremediation
25	Li et al. (2015)	Comparison of 1,2,3-Trichloropropane reduction and oxidation by nanoscale zero-valent iron, zinc and activated persulfate	ZVI, ZVZ, Persulfate
26	Gong et al. (2017)	Combinatorial metabolic engineering of Pseudomonas putida KT2440 for efficient mineralization of 1,2,3-trichloropropane.	Bioremediation
27	Schmitt et al. (2017)	Optimization and validation of enhanced biological reduction of 1,2,3-trichloropropane in groundwater	Bioremediation
28	Wang and Chu (2017)	Cometabolic biodegradation of 1,2,3-trichloropropane by propane-oxidizing bacteria	Bioremediation
29	Coyle et al. (2017)	Use of dilute ammonia gas for treatment of 1,2,3-trichloropropane and explosives-contaminated soils	Ammonia
30	Babcock et al. (2018)	Adsorption of 1,2,3-Trichloropropane (TCP) to meet a MCL of 5 ppt	GAC
31	Porter and Mackey (2018)	Preparing for Change: TCP Overview and Treatment Considerations	Review
32	Kempisty et al. (2019)	Granular activated carbon adsorption of carcinogenic volatile organic compounds at low influent concentrations	GAC
33	Li et al. (2019)	In Situ Persulfate Oxidation of 1,2,3-Trichloropropane in Groundwater of North China Plain	Persulfate
34	Lapeyrouse et al. (2019)	Remediation of Chlorinated Alkanes by Vitamin B-12 and Zero-Valent Iron	ZVI
35	Merrill et al (2019)	Development and Validation of Technologies for Remediation of 1,2,3-Trichloropropane in Groundwater	Review
36	Torralba-Sanchez et al. (2020)	Reduction of 1,2,3-trichloropropane (TCP): pathways and mechanisms from computational chemistry calculations	ZVZ

* Result was identified through a source other than four database search.

Spatial Distribution and Temporal Trends in TCP Treatment Research

In a 2003 report from the World Health Organization, TCP contamination in the hydrosphere was reported in Europe, North America, and Asia (Kielhorn et al., 2003). Globally TCP concentrations in the hydrosphere range from its detection limit (5 ng/L) to > 100, 000 ng/L in both ground and surface waters (Table 2 and Figure 5). An objective

of this study is to reveal spatial trends in TCP research by mapping where treatment studies are taking place in relation to contamination sites (Figure 5).

Table 2 1,2,3-Tricholoropropane distribution in the hydrosphere.

Resource	**Continent**	**Country**	**Source information**	**Maximum concentration** (μg/L)	**Study/Agency**
Drinking Water	Europe	Germany	German cities	0.1	Bauer (1981); Keilhorn et al. (2003)
	North America	Mexico	Not stated	0.18	Gelover et al. (2000)
		United States	California (groundwater), Hawaii (groundwater)	0.24, 0.1	City of Shafter, 2000; Kaua'i Department of Water, 2001
Groundwater	Asia	Canada, B.C.	Aquifer in British Colombia	0.86	Zebarth et al. (1998)
	North America	China	North China Plain	None provided	Li et al. (2015, 2019)
		Netherlands	Potato Plantations	5.6	Lagas et al. (1989); Keilhorn et al. (2003)
		United States	California, Hawaii, New York, etc.	2.7, 2, >100	Burrow et al.; Oki &Giambelluca (1989); Baier et al. (1987)
Surface Water	Europe	Germany	Rivers: Rhein, Emscher, Elbe, and Weser	0.6	BUA, 1993
	Asia	Japan	Rivers: near Osaka	100	Yamamoto et al. (1997)
		Netherlands	Rivers: Rhein, Meuse, Westerscheldt and Northern Delta	2.2	Miermans et al. (2000)
		Slovakia	River: Nitra	1.6	Frischenschlager et al. (1997)

* Note TCP concentration units are in micrograms/L (μg/L)
**TCP source may be agricultural or industrial.
***Data from Keilhorn et. al (2003) and included review papers.

Sixty-five percent (23/36) of papers in this study analyze research conducted in the U.S. followed by the Netherlands (14%, 5 papers) (Table 3). The U.S. and the Netherlands have significant groundwater contamination with TCP connected to agricultural application to orchards, vineyards, and potato crops (Babcock et al., 2018; Samin and Janssen, 2012). Though none of the TCP research papers were published in South America, Africa, or Australia, the global reach of companies manufacturing TCP suggests global contamination (Table 3). Analytical methods used to screen for TCP at very low levels have only been in use since 2002 (SWRCB, 2017). If more countries pass legislation and set regulatory limits, TCP will be detected in more groundwater supplies and a clearer picture of its distribution will emerge.

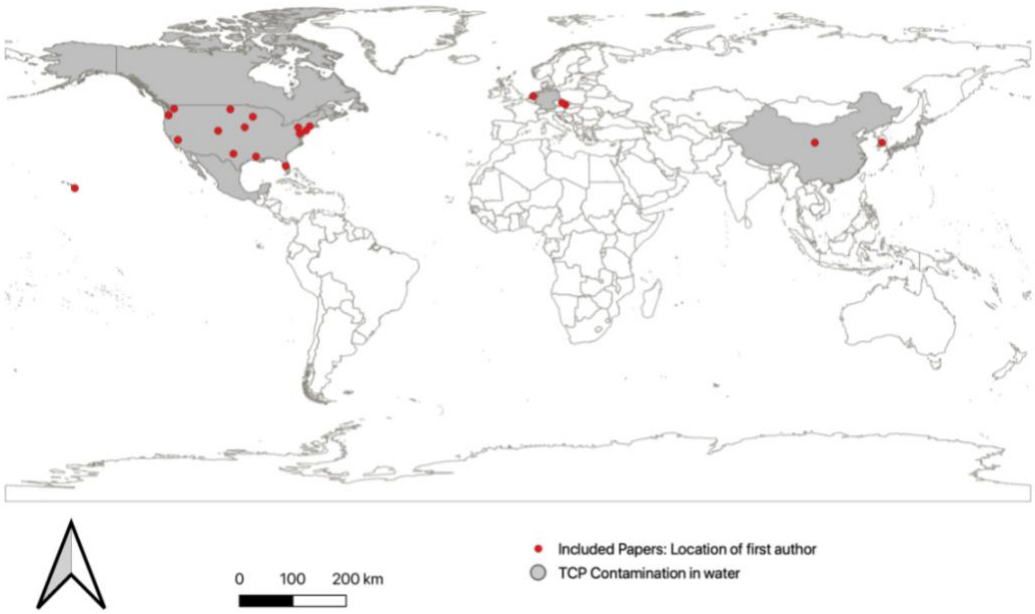

Figure 5 1,2,3-TCP contamination in hydrosphere and location of first author of publication.

Table 3 Primary Researcher location for 36 papers on 1,2,3-tricholoropropane treatment

Location	Number of papers	State/Provence
USA	23	Oregon (6), California (3), Hawaii (2), Pennsylvania (2), Colorado (1), Connecticut (1), Maryland (1), Minnesota (1), Nebraska (1), North Dakota (1), Florida (1), Louisiana (1), Texas (1), Washington (1)
Netherlands	5	
China	4	
Czech Republic	3	
South Korea	1	
Total	**36**	

In California, hundreds of wells tested above the MCL for TCP (5 ng/L). To determine the national occurrence of TCP contamination, U.S. suppliers tested more than 5,000 drinking water wells between 2013-2015 as a part of the U.S. EPA's Unregulated Contaminant Monitoring Rule 3 (UCMR3). TCP levels in 1.4% of those wells were higher than California's Public Health Goal (PHG) associated with an elevated cancer risk (10^{-6}) over a lifetime of exposure. Ninety-seven percent (97%) of TCP detections were in groundwater wells (Porter and Mackey, 2018). More updated information is needed to gain a clearer picture of how widespread TCP contamination is in the U.S.

There appears to be an increasing interest in TCP in recent years. In the five years between 1990-1994, only one TCP treatment study was produced. In contrast, there were eleven studies published in the past five years (Figure 6).

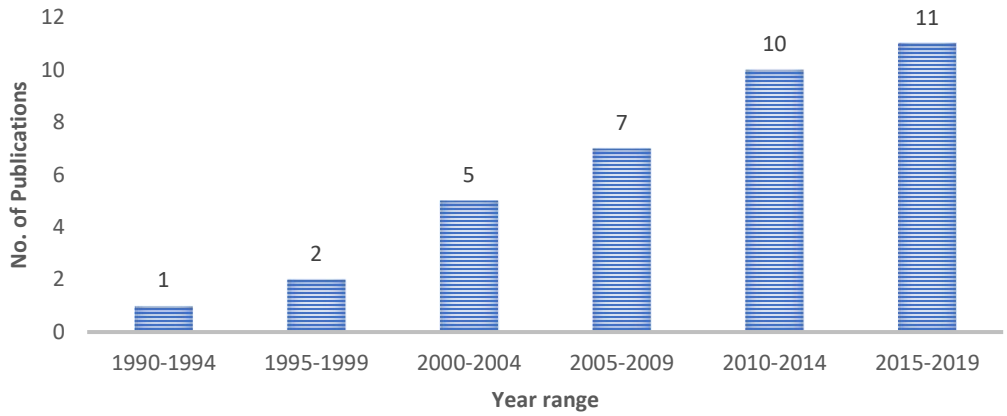

Figure 6 Temporal trends for 36 included 1,2,3-Tricholoropropane treatment papers.

2.3.1 Treatment methods

Of the 36 TCP treatment studies considered for full-text review, 32 were experimental peer-reviewed research papers which fall into two categories: (1) separation-based technologies and (2) degradation-based technologies. The largest number of studies (13, 36%) investigate bioremediation using bacteria with enzymatic activity that can degrade TCP. The next most frequent occurrence of studies is on reductive dechlorination with zero valent iron or zinc (8, 22%) (Figure 7). The U.S. EPA lists available TCP treatment technologies. Ultraviolet radiation combined with oxidation using potassium permanganate, and oxidation processes using ozone are on the EPA's list. However, none of the papers in this review used these treatments (EPA, 2017).

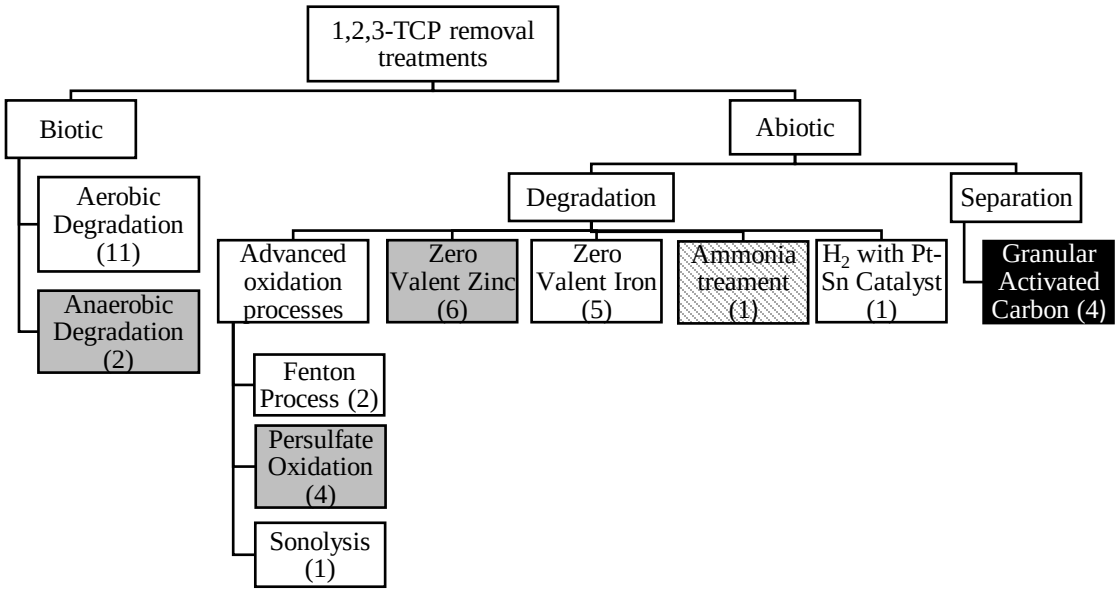

Figure 7 Treatment method, research stage, and number of studies (parenthesis) of the research articles selected for this review. Some papers fall into multiple categories. Stage of testing is noted by shading: full-scale (black), pilot-scale (grey), bench-scale using contaminated soil (hatched), or bench-scale with TCP spiked water (white). Adapted from: Miklos et al. (2018)

Bioremediation

Thirteen studies investigate the use of either aerobic or anaerobic biodegradation with strains of bacteria to dechlorinate TCP. Aerobic biodegradation includes cometabolism with monooxygenase enzymes and hydrolysis mediated by haloalkane dehalogenase (Samin and Janssen, 2012). Anaerobic biodegradation pathways are reductive dechlorination and dihaloelimination, with TCP as the electron acceptor in both cases (Samin and Janssen, 2012). Reductive dechlorination occurs when bacterial enzymes contact chlorinated organic molecules, remove chlorine, and replace it with hydrogen (Samin and Janssen, 2012). Dihaloelimination is the replacement of two adjacent chlorine atoms by an additional carbon-carbon bond (Samin and Janssen, 2012).

Though GAC-based treatments transfer TCP from a liquid to a solid phase, bioremediation degrades TCP to an innocuous alkane. However, bench-scale tests show that partially chlorinated intermediates may form. In the case of anaerobic degradation, dihaloelimation may produce potentially toxic allyl chloride and allyl alcohol both of which are biodegradable in aerobic and anaerobic conditions (Yan et al., 2009). Toxic products from aerobic cometabolic degradation using methane monooxygenase include dichloropropanols (Bosma and Janssen, 1998). Aerobic hydrolysis with dehalogenases produces 1,3-dichloro-2-propanol and 2,3-dichloro-1-propanol; however, both are biodegradable (Samin and Janssen, 2012).

The most frequently studied treatment method, appearing in eleven of thirteen studies, is aerobic enzymatic degradation of TCP, which requires the addition of metabolites (Samin and Janssen, 2012). Aerobic methane-oxidizing bacteria, for example, can cometabolize TCP, but only with added propane (Vannelli et al., 1990). Cometabolism indicates that TCP degradation occurs only in the presence of another organic material serving as the primary energy source. These studies investigate three enzymes: methane monooxygenase, propane monooxygenase, and haloalkane dehalogenase (DhaA) (Samin and Janssen, 2012). Six of the eleven studies use a genetically engineered bacteria which improves enzymatic degradation activity of DhaA by one to two orders of magnitude. The specificity constant (Kcat/Km) indicates catalytic efficiency and is a convenient way to compare the overall ability of an enzyme to convert substrate (in this case TCP) to product (Johnson and Goody, 2011). Kcat/Km values for dehalogenase TCP are reported as high as 1050 s^{-1} M^{-1} using the genetically engineered dehalogenase enzyme DhaA31 compared to 36 $s^{-1}M^{-1}$ [1] for wild type strains (Samin and Janssen, 2012). In a study using the dehalogenase enzyme LinB (used to degrade the pesticide Lindane), Monincová et al. (2007) report a weak specificity constant 0.068 $s^{-1}M^{-1}$. Although low activity limits its current usefulness as a treatment, the degradation, however small, opens a door to using LinB for future protein engineering studies.

Two studies focus on the anaerobic biodegradation of TCP. In 2009, an anaerobic bacterium called Dehalogenimonas lykanthroporepellens (Dhg) was isolated from a TCP contaminated petroleum processing superfund site near Baton Rouge, Louisiana, USA. Dhg can use TCP as an electron acceptor, in addition to other chlorinated alkenes. However, bacterial growth required hydrogen as the electron donor. Maximum dechlorination occurred between pH 7 to 7.5 (Yan et al., 2009). A 2017 study at a site in California's Central Valley shows that Dhg could reduce TCP to meet regulatory levels, even at low initial concentrations (< 2 µg/L), and also showed that reduction continued in

the field for 15-months post injection. That study shows that degradation rates are slower the lower the TCP concentration. Higher inoculum concentrations are needed for reduction, and optimal reduction occurs in a pH range from 7 to 9 (Schmitt et al., 2017).

Zerovalent Iron and Zinc

Eight papers investigated zero valent metals as reductants, namely: iron and zinc to treat water contaminated with TCP. Zero Valent Zinc (ZVZ) is a more potent reductant than Zero Valent Iron (ZVI), reducing TCP at rates one to three orders of magnitude faster (Salter-Blanc et al., 2012). ZVZ successfully degrades halogenated alkanes, which includes TCP, of various sizes (Tratnyek et al., 2010a). ZVZ fully reduces TCP to propane which avoids the accumulation of partially reduced products, but when treated with ZVI, multiple products result, including propane, propylene, and trace amounts of 1-chloro- 2-propene (Klausen et al., 2003; Sarathy et al., 2010).

In Li et al. (2015), the authors used nanoscale ZVI powder in addition to a powder made with zinc and found that there was only negligible TCP degradation, with rates so small the reaction was deemed invalid. Furthermore, Li et al. (2015) concluded that reducing TCP by dechlorination requires a reducing material with a higher surface reactivity than found in ZVI. Additionally, bench tests show that using ZVI to reduce TCP is not feasible due to ZVI's low reductive capability (Klausen et al., 2003; Sarathy et al., 2010; Li et al., 2015).

In multiple bench scale experiments using ZVZ, TCP was removed below detection limits (5 ng/L) for samples ranging in concentration from $30 – 10^5$ micromolar (μM). Kinetics experiments reveal that rate constants normalized for surface area (K_{SA}) were between 10^{-3} - 10^{-2} (L g^{-1} m^{-2}) (Sarathy et al., 2010; Tratnyek et al., 2010b; Salter-Blanc and Tratnyek, 2011). The presence of anions and pH can lead to zinc corrosion and influence the efficiency of ZVZ's TCP reduction ability. Salter-Blanc and Tratnyek (2011) found that in deionized water, TCP degradation rates were the lowest between pH 8-10 and greater at higher and lower pH values, showing a u-shaped curve with optimal rates of degradation at pH extremes. However, this trend was not observed in groundwater tests, in which rates were significantly slowed in alkaline groundwater above pH 7, possibly from the development of a passivating film on the zinc surface. These findings may have implications for the long-term effectiveness and practicality of ZVZ treatment technology for contaminated drinking water wells.

Granular Activated Carbon (GAC)

Hawaii and California have designated GAC adsorption as the Best Available Technology (BAT) to reduce TCP drinking water contamination, but only four research papers in this review focus on GAC. Using carbon to filter out impurities and to neutralize odor and taste in drinking water dates back centuries. GAC filters, which have been used widely in the U.S. for decades (NRC, 1980), are composed typically of finely ground particles of wood, coal, or coconut shells that have been heated in the absence of oxygen and/or chemically treated to create highly sorbable surfaces. GAC can sorb multiple pesticides in addition to TCP and, unlike air-stripping, does not emit TCP into the air (Babcock et al., 2018). However, the U.S. EPA says that TCP has a relatively low affinity for GAC (EPA, 2017).

To test GAC treatment feasibility, three of the four studies used Rapid Small-Scale Column Tests (RSSCTs) and isotherm experiments (Babcock et al., 2018; Harada, 2014; Mital, 2014). RSSCTs demonstrate GAC contaminant removal efficiency with smaller water volumes and shorter contact times than full scale testing (Crittenden et al., 1986). GAC isotherm tests measure the equilibrium concentration of a specific pollutant in contact with a given sorbent. As such, test results reflect the ability of a particular GAC to remove a specific contaminant. The three TCP GAC treatment studies concluded that the variance in GAC performance may be due to the type of raw material used to make the GAC and to the specific chemistry of the source water matrix, including the presence of organic matter and other contaminants (Babcock et al., 2018; Harada, 2014; Mital, 2014). The three studies also share some GAC carbon sources - a coal-derived carbon sold by Calgon called Filtrasorb 400 (F400) and Calgon Coconut Shell Carbon (OLC 12x40).

Of the GACs tested in wells in Hawaii and California, F400 and OLC 12x40 sorbed the greatest amount of TCP before breakthrough to the MCL concentration (5 ng/L), 677 ng/kg and 676 ng/kg respectively (Harada, 2014; Mital, 2014). Jacobi Coconut Shell Carbon was the least effective at TCP removal at all wells tested, regardless of location, by up to one order of magnitude (36-113 ng/kg). No single GAC was effective for all water sources.

Although there was mixed performance, all GAC types lowered TCP effluent concentrations to the 5 ng/L MCL. The total volume of influent treated (number of bed volumes) can differ by up to one order of magnitude depending on the GAC carbon stock selected (Babcock, 2018). Kempisty et al. (2020) used RSSCT to test for reduced sorption due to the presence of other contaminates and dissolved organic matter which often co-occur in groundwater. They calculated the Carbon Use Rate, the mass of carbon needed to treat a volume of water to a target concentration, in this case 0.5 µg/L. At approximately 0.038 lbs/1000 gallons treated, a 15-min Empty Bed Contact Time (EBCT) resulted in earlier breakthrough compared to 7.5-min EBCT, due to desorption caused by dissolved organic matter (Kempisty et al., 2020).

GACs are emptied, reactivated, or replaced when breakthrough concentrations are between 10-50 ng/L. Harada's (2014) data also shows that GAC particle size affects performance – the smaller the particle size (mesh size 170 x 200) the quicker contaminants break through the filtration compared to larger sizes (mesh size 100 x 120). However, particle size performance may be due to the accuracy of the scaling equations used (Harada, 2014). Before the effects of GAC particle size can be fully understood, more information is required.

Persulfate oxidation

This review identified four studies that assess activated persulfate's ability to degrade TCP (Huang et al., 2005; Li et al., 2019, 2015; Tratnyek et al., 2010b). Although the power of mild oxidants (permanganate is one) to degrade TCP is negligible, if the persulfate ion is activated by heat, UV light, ultrasound, or transition metals, the result is a more powerful oxidant. Known as the sulfate free radical (SO_4^-), this oxidant can completely mineralize TCP (Li et al., 2015; Tratnyek et al., 2010b); bench-scale tests show that the reaction kinetics for TCP degradation in the presence of heat-activated persulfate are similar to other chlorinated ethanes (Tratnyek et al., 2010b). However,

Huang et al. (2005) found only 17% TCP degradation in bench testing with heat activated persulfate.

In 2019, a study achieved 61% TCP degradation rates with Fe^{2+} - activated persulfate (Li et al., 2019). Li et al. (2019) tested the in-situ injection of Fe^{2+} - activated persulfate at the pilot-scale in the North China Plain where TCP had leached into the groundwater from the site of a chemical plant. In bench scale tests with Fe^{2+} - activated persulfate, they achieved 50% reduction of TCP in a 24-hour period (Li et al., 2019). But, with pilot scale tests, TCP degradation efficiency was only 8.3%; presumably these lower rates resulted from the presence of other contaminants and compounds in the site's water. Higher reduction rates were seen for aromatic hydrocarbons than in aliphatic hydrocarbons (Li et al., 2019).

Ammonia treatment

This review found one study that used an ammonia treatment to degrade TCP in soil (Coyle et al., 2017). As the authors note, deep subsurface in situ ammonia treatments are currently not feasible, but someday they might also be used in TCP contaminated water (Coyle et al., 2017). Although not in this review, Milchert et al. (2000) demonstrate that ammonolysis can chemically transform waste TCP to 2-chloroallyamine, which is used to manufacture pesticides and pharmaceuticals (Milchert, 2000).

Coyle et al. (2017) report TCP degradation rates ranging from 37-65% at 23^{o}C and from 89-94% at 62^{o}C. Adding dilute ammonia gas (NH_3) to soil raises the pH as it combines with water to produce ammonium and hydroxide ions. This process, called alkaline hydrolysis, has been used to treat soils contaminated with halogenated propanes, explosives, pesticides, herbicides (Coyle et al., 2017). The high pH values can induce a second round of degradation via activation of the enzyme ammonia monooxygenase, capable of co-metabolic TCP mineralization.

Fenton's treatment

Two papers included in this review apply Fenton's reaction to degrade TCP (Hunter, 1997; Khan et al., 2009). The Fenton reaction uses metal ions to increase the oxygen transfer properties of hydrogen peroxide (H_2O_2) (Babuponnusami and Muthukumar, 2014). In acidic conditions, the combination of Fe^{2+}/Fe^{3+} or Zn^{2+} and H_2O_2 produces hydroxyl (•OH) radicals capable of degrading TCP. Although highly effective at oxidizing organic pollutants, this reaction requires careful control of conditions such as pH, temperature, and the iron or zinc/H_2O_2 ratio. In addition, multiple undesirable by-products are produced with this process, 1,3-dichloropropanone; chloroacetic acid, 2,3-dichloro-1-propene, isopropanol, and propionic aldehyde formic acid among them (Hunter, 1997; Khan et al., 2009).

Bench scale experiments show that TCP mineralization is slow. Hunter (1997) reduced TCP by 95% after 14 days of contact with Fenton's reagents. The kinetics follow first order reduction for TCP. Khan et al. (2009) found that given a 20 mg/L solution of TCP in contact with Fenton reagents, 90% of TCP was degraded after 180 minutes and TCP was below detection limits after 240 minutes.

Sonolysis

This review included one study investigating the use of ultrasound to mineralize TCP. In "Sonolysis of Chlorinated Compounds in Aqueous Solution", Lim et al. (2007) used batch tests to estimate reaction rates for a variety of chlorinated compounds, including carbon tetrachloride, trichloroethylene (TCE), and TCP. Sonolysis has been used to remove volatile organic compounds from water (Mukesh, 2012). In solution, ultrasonic waves produce cavitation bubbles which, upon collapse, act as high energy hotspots and produce hydroxyl (•OH) radicals which can oxidize chemical contaminants. The advantage to ultrasound is that it does not require the addition of chemical reagents to capture or degrade pollutants, but it is energy intensive (Wood et al., 2020). Lim et al. (2007) show that TCP can undergo thermal combustion (pyrolysis) inside cavitation bubbles and also that reaction rates are optimal at relatively low temperatures (10^{o}C) and high-power intensity. A pseudo first order kinetic model was used to analyze results. Of the three chlorinated compounds tested, TCP had reaction rates most sensitive to higher temperatures, possibly explained by its high activation energy. (Lim, et al., 2007). Furthermore, depending on the degree of oxidation of the pollutant, undesirable partially oxidized products can be created and require secondary treatment.

Hydrogen-assisted Dichlorination with Pt-Sn Catalyst

In a bench study, Early et al. (2000) investigated the potential for using platinum and tin as catalysts to dechlorinate TCP. They disrupted the carbon-chlorine bond, as per the following two reactions (from Early et al., 2000):

$CH_2Cl\text{-}CHCl\text{-}CH_2Cl + 2H_2 \rightarrow CH_2{=}CH\text{-}CH_3 + 3HCl$
$CH_2Cl\text{-}CHCl\text{-}CH_2Cl + 2H_2 \rightarrow CH_2{=}CH\text{-}CH_2Cl + 2HCl$

Early et al. (2000) explain how changing specific parameters of the kinetics experiments affects the production of byproducts. Their study varied the amounts of C, Pt and Sn exposed to a reaction mixture of TCP (3,000 ppm) and H_2 (15,000 ppm). Dechlorination products included propane, propene, allyl chloride, and dichloropropene. Catalysts with Pt:Sn ratios of 9:1 and 6:1 exhibited a higher relative hydrogenation activity than monometallic Pt/C. Though Pt/Sn C catalyzed hydrogenation reduced TCP, the Early et al. (2000) study did not establish reaction rates nor removal percentages. In short, the feasibility of Pt/Sn C catalyzed hydrogenation as a treatment technology and for limiting the production of undesirable byproducts has yet to be determined.

2.3.2. TCP Reviews, reports, and treatment overviews

This review found one report (Tratnyek et al., 2010b), one overview (Porter and Mackey, 2018), and two reviews of TCP treatments published in peer reviewed journals (Samin and Jansen, 2012; Merrill et al., 2019) Neither of the reviews are systematic and one is focused only on select elimination technologies. A summary of key findings is in Table 4.

In a 2010 report for the Strategic Environmental Research and Development Program (SERDP), Tratnyek et al., (2010b) determined rates and products of major types of natural and engineered in situ TCP degradation technologies (with the exception of bioremediation) and investigated optimal zinc selection and reduction conditions.

Tratnyek at al. (2010b) found industrial and reagent grade zinc effective at dechlorinating TCP in deionized water.

The Water Research Foundation (WRF) funded overview of TCP treatment studies found that air stripping is not a cost-effective way to meet low regulatory levels (Porter and Mackey, 2018). One of the WRF studies evaluated the TCP sorption performance of four different types of GACs and found significant differences in sorption capacity, underscoring the importance of choosing the right GAC carbon stock (Mital, 2014; Harada, 2014; Babcock., 2018). Another WRF study found that temperature plays a role in GAC efficiency, with adsorption capacity at 35°C approximately 1.5 times the adsorption capacity at 23°C (Porter and Mackey, 2018).

In their 2012 study, Samin and Janssen (2012) reviewed abiotic and biotic TCP transformations and concluded that anaerobic reductive dechlorination may be the best option for in situ treatment of contaminated water at low concentrations (TCP < 1mg/L). Although aerobic transformations are thermodynamically feasible, co-metabolic transformations can produce toxic products. No naturally occurring aerobic organisms have been found that can oxidize TCP and use it to support growth. This may be due to the rare occurrence of the DhaA gene in nature (Samin and Janssen, 2012). However, the construction of recombinant bacterial strains with enhanced DhaA activity (Bosma et al., 2002) may increase the practicality of this technology as a full-scale treatment. Nevertheless, due to low levels of homogenous oxygen in wells contaminated with TCP, in situ aerobic transformations of TCP in the subsurface may not be feasible (EPA, 2013).

Table 4 Summary of 1,2,3-Tricholoropropane treatment reviews and reports.

Author, year	Number	Research focus	Key Findings
Tratnyek et al., 2010b	n/a	• TCP degradation pathways: hydrolysis, elimination, reduction, oxidation • ZVI, ZVZ, oxidation methods	• Using reductive chlorination to degrade TCP, ZVZ treatment is offers more complete degradation than ZVI • TCP mineralization achieved with activated persulfate but not with mild oxidants like permanganate • Industrial-grade ZVZ degrades TCP as fast as reagent-grade
Samin and Jansen, 2012	30	• Natural abiotic degradation and biodegradation	• Full-scale TCP bioremediation is feasible if strains are found or engineered with high activity towards TCP biodegradation
Porter and Mackey, 2018	n/a	• Treatment to meet low regulatory requirements	• GAC seems to be the best available technology for TCP removal; media replacement frequencies will influence design of new treatment facilities.
Merrill et al., 2019	25	• Overview of the benefits and limitations of treatments • Specifies research scale	• In situ chemical reduction (ISCR) and bioremediation (ISB) show the most potential for TCP treatment. • Since GAC has a low sorption capacity for TCP carbon selection is important. The water matrix influences GAC efficiency, site studies are needed for high removal rates and cost efficiency.

In the most recent review of TCP treatment options, Merrill et al. (2019) found that in situ Chemical Reduction (ISCR) and in situ Bioremediation (ISB) show the most

potential for remediation. ISCR using ZVZ has been tested in the field and in a pilot scale test at Camp Pendleton in Oceanside, California where ZVZ was directly injected underground and then monitored. Several ongoing ISB pilot tests at confidential test sites in California's Central Valley show encouraging results. After an initial six-month lag phase, ISB reduced TCP concentrations below 5 ng/L (Merrill et al., 2019).

2.3.3 Identification of TCP treatments

This study aimed to determine the most effective TCP treatment and/or remediation methods. An objective was to identify the types of groundwater treatments for TCP being researched. Treatments can be broadly divided into separation-based and elimination-based technologies. There is one ex situ separation-based technology: GAC, and eight elimination-based technologies: (1) Bioremediation; (2) Zero Valent Zinc; (3) Zero Valent Iron; (4) Persulfate Oxidation; (5) Fenton's treatment; (6) Ammonia treatment; (7) Hydrogen Assisted Dechlorination; and (8) Sonolysis.

Because degradation parameters are unique to a specific treatment technology (Table 5), direct comparison of treatment types is difficult. As large wells impacted by TCP may take decades to treat, sustainability should be a reported factor in the "success" of a treatment technology. For example, GAC experimentation involves an RSSCT test to estimate the total number of bed-volumes or empty-bed contact time intervals that different GACs can treat before they are replaced or regenerated. Because of low-moderate sorption affinities between GAC and TCP, TCP removal percentages are high (90-99%). Nevertheless, GAC media replacement rates might be cost prohibitive (Porter and Mackey, 2018). The cost of frequent media replacement might especially deter small water treatment systems from adopting this technology (Bereskie et al., 2017).

2.3.4. Scale of testing and summary of removal information

Another objective of this review is to determine which TCP remediation methods have been field tested with TCP-contaminated groundwater; those limited to bench tests with water spiked with TCP; those that have undergone pilot testing; and those that are in full-scale operation (Figure 4 and Table 5). GAC is currently in use for TCP removal by at least seven water utilities in California, and some water systems in Hawaii have used GAC for at least 30 years, treating several hundred millions of gallons of water daily (Babcock et al., 2018; Merrill, 2019).

While several treatments show verifiable improvement in water quality, others need confirmation (Table 5). Merrill et al. (2019) describe bioremediation pilot tests that succeeded even in wells with low (<2 μg/L) initial concentration of TCP and in raw source water (Merrill et al., 2019). Pilot tests that use ZVZ to reduce TCP also show encouraging results. Direct injection of commercially available ZVZ significantly reduces TCP in groundwater. Since ZVZ is a powerful oxidant, the occurrence of partially chlorinated byproducts is not observed. Another in situ pilot study reported on the application of activated persulfate in a contaminated site in the North China Plain (Li et al., 2019). TCP degradation was between 30%–45%, depending on the well, but because sulfate concentrations increased, concerns remain about potential secondary water impacts (Li et al., 2019). Though Fenton's process is effective at oxidizing TCP, no groundwater samples have been tested with this technology (Merrill et al., 2019). Lastly, sonolysis and hydrogen assisted dechlorination showed success in some bench-level

testing, but field tests are needed to confirm TCP degradation in contaminated source water.

Although the natural attenuation of TCP is thought to be minimal under neutral conditions, alkaline conditions and higher temperatures promote TCP hydrolysis (Tratnyek et al., 2010b). Since pH influences removal efficiency, studies that include pH conditions in methodology are included in Table 5, and if an objective of the study was to determine optimal pH range for a particular treatment, it is reported in bold. Additional information regarding pH for each included study is in the supplementary data Table S11. Except for hydrogen assisted dechlorination, there was at least one paper in each treatment category which listed the pH conditions of the experiment. Fenton's treatment, persulfate oxidations and sonolysis occur at low pH conditions; for anaerobic bioremediation the pH range is closer to neutral (7-7.9). Studies optimizing removal rates of ZVZ as a function of pH show mixed effects, Salter-Blanc and Tratnyek (2011) show two optimal peaks for ZVZ treatment one below pH 8 and the other above pH 10. However, with groundwater samples pH < 7 was optimal possibly due to a passivating surface which may form on zinc in alkaline conditions (Salter-Blanc et al., 2012).

Table 5 Summary of articles organized by TCP treatment type

Treatment type	#	Maximum reported removal information	pH conditions or optimal range (bold) [a]	Article citations	Scale of research
Bioremediation (aerobic)	1 1	kcat/km = 1,050/M-sec	6.9-9.4 5.5-6.0 and 8.0–9.0	Vannelli et al., 1990; Bosma and Janssen, 1998; Bosma et al., 1999; Bosma et al., 2002; Pavlova et al., 2009; Monincova´ et al., 2007; Kurumbang et al., 2014; Li and Shao, 2014; Samin et al., 2014; Gong et al., 2017; Wang and Chu, 2017	Bench
Bioremediation (anaerobic)	2	0.407 mg/L/Day	**7.0–7.5; 7-9**	Yan et al., 2009; Schmitt et al., 2017	Bench, Pilot
Zerovalent Zinc	6	Up to 100% (non-detect level) 10^{-3} L m^{-2} h^{-1}	**>10 or < 8** **Groundwater <7**	Sarathy et al., 2010 [b]; Tratnyek et al., 2010b, Salter-Blanc and Tratnyek, 2011; Salter-Blanc et al., 2012; Hui et al., 2015 [b]; Torralba-Sanchez et al., 2020	Bench, Pilot
Zerovalent Iron	5	Negligible	9.2 and 11	Vikesland et al., 2003; Sarathy et al., 2010 [b]; Tratnyek, 2010b; Hui et al., 2015 [b]; Lapeyrouse et al., 2019 [b]	Bench

Granulated Activated Carbon	4	90- 99 % removal	7-9.8	Mital, 2013; Harada, 2014; Babcock et al., 2017; Kempisty et al., 2018	Bench, Full Scale Use
Fenton	2	90-90% removal	**2-4**	Hunter, 1997; Khan 2009	Bench
Persulfate oxidation	4	50 % reduction in 24 hours; 2.7 x 10^6 $M^{-1}s^{-1}$	2.1-3.0	Huang et al., 2005, Tratnyek et al., 2010b; Li et al., 2015, Li et al., 2019	Bench, Pilot
Ammonia Treatment	1	37-65% at 23ºC 89-94% at 62ºC	8-10	Coyle et al., 2017	Bench
H_2 Assisted dechlor-ination	1	None stated	n/a	Early et al., 2000	Bench
Sonolysis	1	0.00960 min^{-1}	3	Lim et al., 2007	Bench

[a] if determining optimal pH was a research objective, it is bold. Otherwise, pH values were in methods.
[b] Both iron and zinc

2.3.5 Chemical byproducts

A third objective of this review is to determine if chemical byproducts are produced by different TCP treatment types, and if so, what kinds. Co-metabolic biodegradation using aerobic bacteria, reduction with ZVI, and Fenton's treatment all produce undesirable byproducts that could limit their adoption (Samin and Janssen, 2012; Sarathy, 2010; Khan 2009). Technologies tested less frequently, such as sonolysis; ammonia treatment; oxidation with strong oxidants; and with hydrogen assisted dechlorination, have not had a full analysis of their chemical byproducts (Lim et al., Coyle et al. 2017; 2007; Li et al., 2019; Early et al., 2000). Future research may determine if these technologies create undesirable byproducts. Although TCP sorption onto GAC does not cause chemical changes in TCP, it does produce spent materials which either must be regenerated with heat or replaced and disposed of as waste (Harada, 2014).

2.3.6 Further research

A final objective of this study is to identify opportunities for future study. Research is needed on changes in microbial populations due to exposure to TCP, the possible byproducts of sonolysis degradation and secondary water quality impacts from the use of activated persulfate treatments. Another area for further research is finding an optimal combination of GAC characteristics to apply to wells contaminated with TCP. Meanwhile, for maximum usability site-specific GAC TCP removal data should include the presence of co-contaminants, influent and effluent concentrations, bed volume quantities, and the sorption amount normalized to mass of GAC used (mg/kg) (supplementary information Table S6). Overall, a systematic reporting of contaminate removal data (influent and effluent concentrations, removal percentages, and the use of standard units) would facilitate comparisons of how effective certain technologies are at separating or eliminating TCP from water.

Other than coconut shells, no other agricultural waste product, such as almond shells which are abundant in California's Central Valley, have been studied. Such non-

traditional, less commercial, and more sustainable carbon alternatives might prove effective. Furthermore, with the exception of the GAC studies, treatment cost comparisons are absent from the literature. Cost and sustainability comparisons would be helpful for LIMICs with TCP contamination. The U.S. EPA provides treatment cost worksheets for small (<200 connections) and large (>200 connections) using the work breakdown structure (WBS) model to account for permits, capital costs, and annual operation and maintenance. Current calculators available for GAC vary substantially based on well type, design, location, and flow rate (EPA, 2020). Finally, future research and monitoring is needed to reveal the extent of TCP contamination in other countries. A limitation of this study may be because searches for this review were performed in English.

2.4 Conclusion

This research supports two United Nations Sustainable Development goals: Goal 6, Clean Water and Sanitation targeting safe and affordable drinking water for all by reducing pollution, and Goal 3, Good Health and Well-being through a reduction in illnesses from pollution (UN, 2015). The long-term health consequences of prolonged exposure to TCP are unknown, but experiments indicate that TCP in drinking water is a probable human carcinogen. California has set low limits for TCP—the Maximum Contaminant Levels and Public Health Goals are set as low as 5 ng/L and 0.7 ng/L respectively. Meeting these low regulatory limits demands efficient, low-cost, and environmentally sustainable treatment technologies.

Of the treatment technologies included in this systematic review, GAC, bioremediation, and ZVZ show the most promise for reducing TCP levels and meeting regulatory requirements for drinking water. GAC is in full-scale use in water systems in Hawaii and California and anaerobic biodegradation and chemical reduction by ZVZ are in pilot-scale use in California. Although data is limited, strong oxidants like persulfate also appear to remove high levels of TCP (Li et al., 2015). An ammonia treatment is used in only one soil study but shows high rates of TCP degradation (Coyle, 2017). In bench and field tests, GAC reduces TCP levels to as low as 5 ng/L in groundwater samples. However, since TCP has a low to moderate adsorption capacity for GAC, the technology requires frequent media replacement and refilling, limiting its practicality. Site specific testing is necessary to establish co-contaminates and water chemistry for optimal GAC selection to decrease the operational costs of using this technology.

Although no information about TCP contamination was found in South America, Australia, and Africa, there is evidence of widespread global contamination of TCP in the hydrosphere. A complete global map of TCP contamination requires more sampling, testing, and monitoring. Agricultural regions, chemical manufacturing sites, and military establishments are all areas of concern, especially if drinking water is drawn from groundwater.

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2.5 Chapter 2 References

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Chapter 3. Using Machine Learning to Predict 1,2,3-Trichloropropane Contamination from Legacy Non-Point Source Pollution of Groundwater in California's Central Valley[(B)]

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Abstract

1,2,3-tricholoropropane (TCP) is an impurity common in nematicides applied to agricultural soils from the 1940s to the 1980s. Evidence from animal studies indicates that TCP is a probable human carcinogen. TCP leaches through the soil into groundwater where it persists and contaminates thousands of wells in Asia, Europe, and North America. In California, TCP contaminates drinking water wells, with the highest levels of TCP beneath agricultural land used to grow grapevines. This study performs a mass balance and evaluates the ability of three types of tree-based machine learning models to predict TCP concentration in California's Central Valley aquifer system: classification and regression trees (CART), Random Forest (RF), and Boosted Regression Trees (BRT). To construct the models, multiple spatial explanatory variables were used, including historical agricultural land use data, irrigation levels, precipitation, soil type, groundwater age, redox state, and the presence of the co-contaminant nitrate. To estimate the amount of TCP applied to farmland in California, state historical pesticide and land use documents were used in the mass balance. Between 110,000 and 4,300,000 kg of TCP are estimated to have accumulated in the subsurface. Machine learning models indicate that the most important explanatory variables to predict TCP contamination of groundwater are precipitation, redox state, and the presence of the co-contaminant nitrate. Additionally, a 1000-m buffer area offers a slightly higher predictive performance as compared to 500-m and 1500- m buffers. Furthermore, the RF model outperforms CART and BRT for predictive performance. Finally, modeling using decision trees can predict TCP contamination levels in areas where monitoring is lacking, help target future TCP monitoring efforts, and aid in identifying areas to avoid when drilling new drinking water wells.

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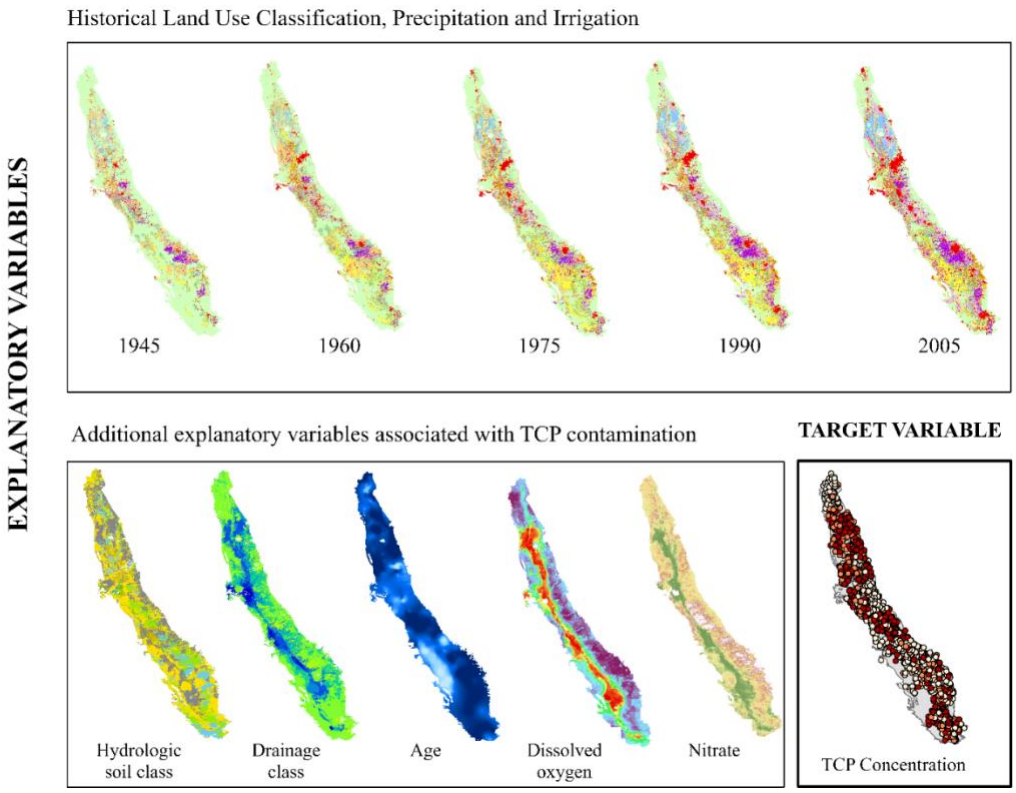

Figure 8 Graphical Abstract

3.1 Introduction

For nearly forty years, 1,2,3-trichloropropane (TCP) was applied in agricultural regions in California, in other areas in the US, and in other parts of the world (Hauptman and Naughton, 2021a). TCP is a probable human carcinogen (USNTP, 1993). Even though California banned TCP decades ago, TCP is still found in groundwater because of its persistent qualities, especially in rural parts of the Central Valley. This study describes an effort to approximate the amount of TCP persisting in California's groundwater using mass balance and multiple tree-based machine learning models. While other studies have applied machine learning to predict a variety of contaminants at regional, national, and global scales, this is the first study to use such methods for a volatile contaminant like TCP (Ibrahim et al., 2022; Ling et al., 2022; Mosavi et al., 2021; Ransom et al., 2017b, 2022).

By predicting the amount of TCP contamination and the likeliest locations where it may be found, this study contributes to a greater understanding of how to address one of environmental engineering's grand challenges in the 21st century, providing a safe and sustainable water supply for a growing global population, while also addressing the United Nations Sustainable Development Goals #3 and #6 (NASEM, 2019; UNSDG, 2015). Since more than a third of the world's freshwater resources are underground and demand for that water is growing in urban and peri-urban communities, the UN considers groundwater extraction the only way to provide basic water needs to much of the world's rural population (UN, 2022). The challenge of supplying potable well water is exacerbated not only by its scarcity, but also by the widespread presence of

anthropogenic non-point source pollutants from livestock waste, soil amendments, and pesticides (Harter, 2003; UN, 2022). In the United States Geological Survey (USGS) 2013–2018 National Water-Quality Assessment (NAWQA), 128 pesticides and degradants were detected in wells sampled nationwide (Bexfield et al., 2020). TCP was an impurity present in at least two popular fumigant pesticides, Telone and D-D, that targeted soil nematodes (Burow et al., 2019), and has been detected in groundwater in Asia, Europe, and North America, (Hauptman and Naughton, 2021a). In 13 U.S. states and in Puerto Rico it is known that hundreds of drinking water wells are contaminated, but because TCP is difficult and costly to monitor, little is known about how other parts of the world are affected (Hauptman and Naughton, 2021b). In rural agrarian areas in the Central Valley of California, where public and domestic water is drawn primarily from underground sources, there are public health concerns over contaminated wells (Fernandez-Bou et al., 2021).

TCP is a highly toxic agricultural pollutant of prime concern, and it has been the focus of numerous studies (Hauptman and Naughton, 2021a). Since TCP persists in groundwater and is recalcitrant, most of those studies explore ways of removing TCP from water. The studies have had varying degrees of success and various stages of implementation. The most represented technologies in those studies included biodegradation, zerovalent transition metals, and granular activated carbon (GAC), and are either fully deployed by water systems or being tested in the field. (Hauptman and Naughton, 2021a). In a 2019 study, Burow et al. identified land use, soil and aquifer material, well type, redox state, and relative groundwater age as characteristics significantly associated with elevated TCP levels in California's groundwater (Burow et al., 2019). However, these studies do not use these explanatory variables to locate the sites where TCP might be found. To fill this knowledge gap, we apply hybrid machine learning and a GIS mapping approach.

The other major body of TCP studies focuses on its toxicology. Since synthetic chemicals like TCP are among the world's most toxic pollutants, regulators often set Maximum Contaminant Levels (MCLs) low (Kearns, 2012). A 1996 study showed that TCP delivered orally to mice and rats causes tumors to develop in multiple organs including the liver, stomach, and kidneys (La et al., 1996). Since numerous studies suggest that TCP is a powerful human carcinogen and may damage fertility (Irwin et al., 1995; Kielhorn et al., 2003; USEPA, 2009), California set the MCL for TCP at its lowest analytical limit, 0.005 μg/L (SWRCB, 2022).

Because of TCP's toxicity, it is imperative that communities know where TCP-contaminated groundwater is located. However, since TCP has not been in use for more than forty years, locating TCP contamination sites can be especially difficult. The difficulties in locating TCP sites are compounded by a lack of area-specific historical land-use records and massive changes to the Central Valley landscape (CDFA, 1970–1983). Although previous studies have focused on treatment technologies and the toxicity of TCP, none have looked at quantifying the amount of TCP in groundwater nor methods to predict TCP contamination levels, both of which are critical to addressing this problem in unmonitored areas of the world. A previous mass balance for nitrate in California considered multiple historic nitrate stocks and flows (Rosenstock et al., 2014). Although the State of California has monitored TCP levels in groundwater for decades (GAMA, 2021), estimates of how much TCP was applied to and remains in the environment from

non-point agricultural use are absent from the literature. Therefore, this is the first study that uses mass balance to estimate the amount of TCP in California groundwater and train decision tree machine learning models to spatially predict TCP concentrations in groundwater. Widespread TCP application occurred between the 1940s and the 1980s (Burow et al., 2019) but statewide pesticide use reports (PUR) and county-by-county records began in 1970. This study uses the existing years (1970–1984) to calculate a mass balance that approximates TCP's accumulation in groundwater per acre of treated cropland and provides high and low estimates given the range of TCP impurity levels in the literature.

To address the lack of worldwide monitoring data for TCP contamination, we use hybrid GIS and machine learning models built from spatial predictor variables. Spatial explanatory layers were used to construct a predictive model using three different types of decision trees to predict TCP contamination in groundwater. Although high in computational costs, decision trees can handle complex data sets and many predictor variables.

The goal of this study is to use mass balance and hybrid GIS machine learning models to predict TCP concentration levels in groundwater. Our research question asks if the superiority of boosted regression trees (BRT) at predicting groundwater nitrate levels will hold against other machine learning models for predicting TCP (Nolan et al., 2015; Ransom et al., 2017a). Specifically, this research tests if BRT will outperform Random Forest (RF) and single Classification and Regression Tree (CART) models for predicting TCP concentration in groundwater. To provide context for the accumulation of TCP in the study site, we use historical data and mass balance to estimate the extent of the TCP problem in the Central Valley of California. Our research objectives are (1) to use a mass balance approach to estimate quantities of TCP that have leached beyond the root zone in California's soils to cause groundwater contamination; (2) to apply machine learning to predict TCP concentration from explanatory variables from previous research using training and testing data for validation; (3) to rank explanatory variables in order of predictive importance; (4) to compare the prediction performance of multiple regression models and buffer zones using error metrics; (5) to determine which crop types may be more highly associated with median TCP well concentration; and (6) to compare TCP prediction maps with disadvantaged community (DAC) delineations to determine if areas with high-modeled TCP contamination are more likely to occur in DACs. Ultimately this research approach could be used to approximate TCP levels in rural unmonitored groundwater wells beneath existing or former croplands that may have been treated with fumigants containing TCP. The methodology used in our research could be modified for application in other areas of the United States and globally.

3.2 Methods

3.2.1 Study area

The study area is the Central Valley Aquifer Region (CVAR) of California in the United States, an area of approximately 53,000 km^2 (Figure 9). The Central Valley is comprised of two adjacent valleys, the Sacramento Valley to the north and the larger San Joaquin Valley to the south. The Central Valley is surrounded by four mountain ranges: the Coast Range to the west, the Sierra Nevada range to the east, the Cascade Mountains to the north, and the Tehachapi Mountains to the south. An alluvial trough, the valley is

primarily drained through the Sacramento - San Joaquin Delta. With a semi-arid to arid climate with higher average annual precipitation in the north than in the south, the CVAR is one of the most heavily pumped aquifers in the nation; only the Ogallala Aquifer in the High Plains region meets a heavier demand (Lovelace et al., 2020). Producing approximately one-quarter of the nation's food, the Central Valley is the most productive agricultural area in the United States and one of the most important agricultural production areas globally (Faunt et al., 2016; USGS, 2023) The region relies on groundwater withdrawals for irrigation, industry, and household use (Ghasemizade et al., 2019). Groundwater pumping in the CVAR surpasses natural recharge from rain and streamflow by 2 billion cubic meters per year and in dry years overdraft rates are even higher due to less recharge and an increase in withdrawals to supplement the smaller volume of available surface water (Faunt et al., 2016; Medellín-Azuara et al., 2015).

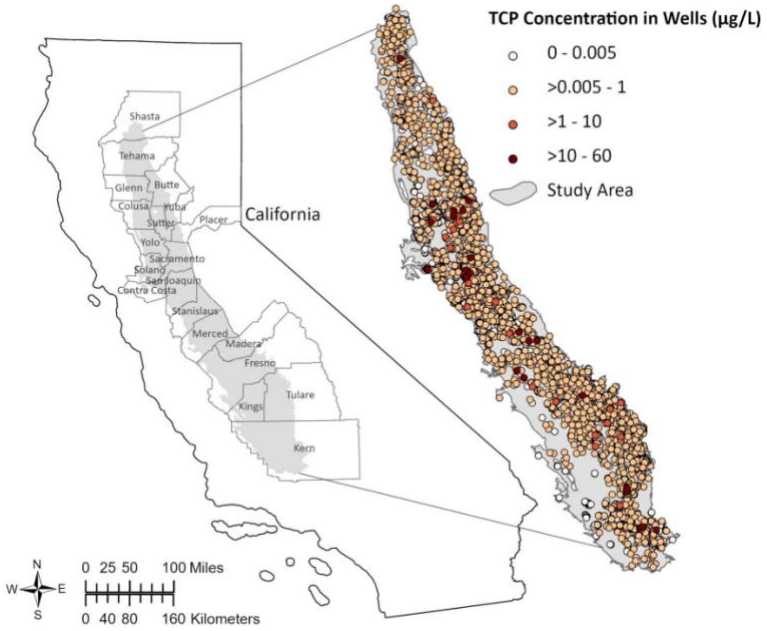

Figure 9 Location of wells contaminated with 1,2,3-trichloropropane (TCP) (GAMA, 2021) in the Central Valley Aquifer Region (California, USA) used for model development. State and county boundary shapefiles are from the California Department of Technology Open Data Portal (CDT, 2019). Figure created by author.

3.2.2 Mass balance estimate for TCP accumulation in the study area

This study approximates TCP loading into California groundwater to provide context to the machine learning model and evaluate the scope of the problem in the study area. Three factors were used to estimate groundwater TCP loading from non-point agricultural sources: (1) the estimated total acreage of cropland treated over a 30-year application period; (2) estimates for TCP loading from fumigant application based on historical records in which a high (7% by mass) and low (0.17% by mass) TCP approximation were used; and (3) a mass balance for applied TCP transport out of the root zone based on TCP's physicochemical properties and transport behavior in soil.

This mass balance model (Figure 10) focuses on TCP's application and diffusive transport out of the root zone. Fumigants rapidly volatilize at ambient temperatures and

pressures and, as vapor phase solutes, they diffuse through soil gas space while partitioning between the water and solid phases. Inputs (flux A in 10) used to estimate the yearly TCP flux, or loading (ṁ, mass per year per acre of cropland), are derived from the California Department of Food and Agriculture Historical Pesticide Use Reports (PUR) (CDFA, 1970-1984). The PUR for 1970–1983 indicates that farmers annually applied a mean of 3,447,629 pounds of fumigants containing TCP (both Telone and D-D mix) to a mean of 50,807 acres of cropland.

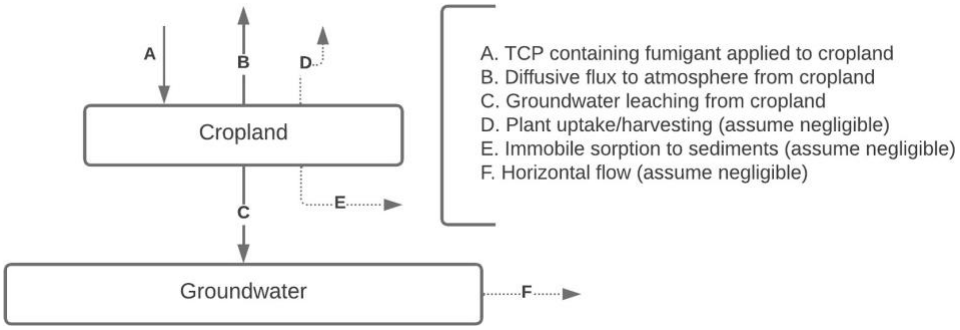

Figure 10 Stocks and flows for non-point source 1,2,3-trichloropropane (TCP) groundwater loading (C) calculation: C = A - B.

Mass balance outputs include upward diffusion of gaseous TCP to the atmosphere (flux B) and downward diffusion toward groundwater (flux C). TCP losses due to plant uptake, surface runoff, and aqueous leaching were assumed negligible. The following equations were used to estimate the accumulation of annual TCP in the subsurface and then applied over a 30-year application period during which TCP containing fumigants were in use.

(1) Groundwater Accumulation = Mass flux - Diffusion to atmosphere - Diffusion to deeper soil:

$$\frac{dC}{dt} = \frac{\dot{m} - \left[\frac{A \times Da(\text{Cair soil layer 1} - C^{atm})}{Z^1} + A \times Da\frac{(\text{Cair soil layer 2} - \text{Cair soil layer})}{Z^2 - Z^1}\right]}{Ra}$$

(2) $Ra = V(n \times \Theta a + n \times \frac{\Theta w}{KH} + \rho b \times \frac{Kd}{KH})$

(3) $C_{initial}^{air} = \frac{\dot{m}}{Vt} \times Ra$

The exact number of years that TCP-containing fumigants were applied is unknown and historical application records are not available prior to 1970, but the literature suggests the late 1940s to early 1980s as a timeframe (Hauptman and Naughton, 2021a). Using PUR data, we can estimate the average mass flux (ṁ) in grams/year and area (A) in meters^2 for thirty years (CDFA, 1970-1984). The TCP concentration is estimated from the PUR records of the approximate amount of Telone and D-D applied in pounds and the area of land (Supplementary Material (SM) Table S1). The combined

application for D-D mixture and Telone for the year 1975 was used as a representative sample for the yearly application amount.

From equation (1) above, D_a (m^2/year) is the estimated diffusion coefficient for TCP in air using the Hayduk and Laudie method at 20 °C (USEPA, 2021). We assume that the fumigant containing TCP volatilized after application, followed by partitioning into different phases based on physicochemical properties (SM Table S2). C is the TCP concentration in air, which was obtained by dividing the mass loading ($\dot{m}$) by the product of the area of treated land and by a retardation factor (Ra) accounting for TCP partitioning to air, water, and soil. Z is the depth of the topsoil layer, V is the volume of the soil layer, n is the porosity, Θ_a is the dimensionless volumetric air content, Θ_w is the dimensionless volumetric water con- tent, K_H is the dimensionless Henry's constant, ρ_b is the bulk density of soil, and K_d is the soil adsorption coefficient.

3.2.3 Machine learning workflow and software

The main procedural steps to this machine learning model are (1) data collection and preprocessing; (2) data partitioning and tuning; (3) data evaluation and prediction; and (4) visualizing predictions on a gridded map surface (Figure 11). ArcGIS Pro v. 2.8.2, a geographic information system, was used to spatially link explanatory variable map layers to the target variable and to visualize the final model prediction. R computing software v. 4.2.2 was used for modeling and statistical analysis. Specifically, the R package caret v. 6.0–93 was used to partition data, tune hyperparameters, train models, and create statistical com- parisons (Kuhn et al., 2018). Built and named for Classification and Regression Training, caret has built-in functions for data preparation, tuning, training, and evaluating multiple types of machine learning algorithms. Three of these off-the-shelf caret learning algorithms were compared in this study: 'rpart2' – a CART model; 'rf' an RF model; and 'gbm' – a BRT model. The raster package v. 3.6–20 was used to apply the models to raster stacks of the study area to predict TCP levels throughout the Central Valley (Hijmans and van Etten, 2012).

3.2.4 TCP data selection and pre-processing

We collected TCP well data from the Groundwater Ambient Monitoring and Assessment (GAMA) Program. In 2000, the State Water Resources Control Board (SWRCB) GAMA database made groundwater quality data available to the public. The SWRCB GAMA Groundwater Information System (GeoTracker) aggregates water quality data from various sources including the Department of Pesticide Regulation, the Department of Water Resources, the USGS priority basin project, and the National Water Information System (SWRCB, 2023). Groundwater is analyzed for TCP concentration using purge and trap capillary gas chromatography coupled with mass spectrometry (U.S. EPA method 524.2).

California law dictates that public water systems monitor for TCP in their water supplies four times per year since the state adopted a maximum contaminant level of 0.005 μg/L (SWRCB, 2022). This study used data from all available well categories from 1990 to 2021. TCP levels fluctuate with groundwater depth and season but since TCP has a half-life on the order of hundreds of years, the mean value of all available measures for an individual well was used for this study (Pagan et al., 1998). Additionally, this analysis uses all available well-point data for the CVAR. The region includes 13,797 wells with a

range of TCP concentrations from 0 to 16,000 µg/L. Measurements at or exceeding three standard deviations from the mean were removed as outliers, reducing the data set to 13,314 wells with a maximum concentration of 60 µg/L TCP. Since the detection limit (DL) for TCP is 0.005 µg/L, entries of zero in the GAMA data set were changed to half of the detection limit value DL/2 (0.0025 µg/L) to avoid the unwarranted treatment of non-detects as zero (Helsel, 1990). Finally, the TCP concentration was $\log_{10}$ transformed to achieve a more normal distribution before modeling.

When assigning explanatory variables to well points, we considered multiple buffer sizes. A 2009 USGS study indicated that a 500-m circle is adequate for assigning land use and calculating the statistical correlation between urban land use and the occurrence of volatile organic compounds in wells (Johnson and Belitz, 2009). A 500-m buffer was also used as the optimal buffer size to relate nitrate concentrations and agricultural land use categorization surrounding a well for the US National Water Quality Assessment Program (Koterba, 1998). However, since a 2019 machine learning study showed that a 1000-m buffer had the highest predictive performance for nitrate in groundwater (Knoll et al., 2019), larger buffer zones were also considered. For the present study, three different circular buffer areas were evaluated with radii of 500, 1000, and 1500 m for the attribution of spatial explanatory variables to well sites, and the predictive performance of these three buffer zones was compared (SM Figure S3).

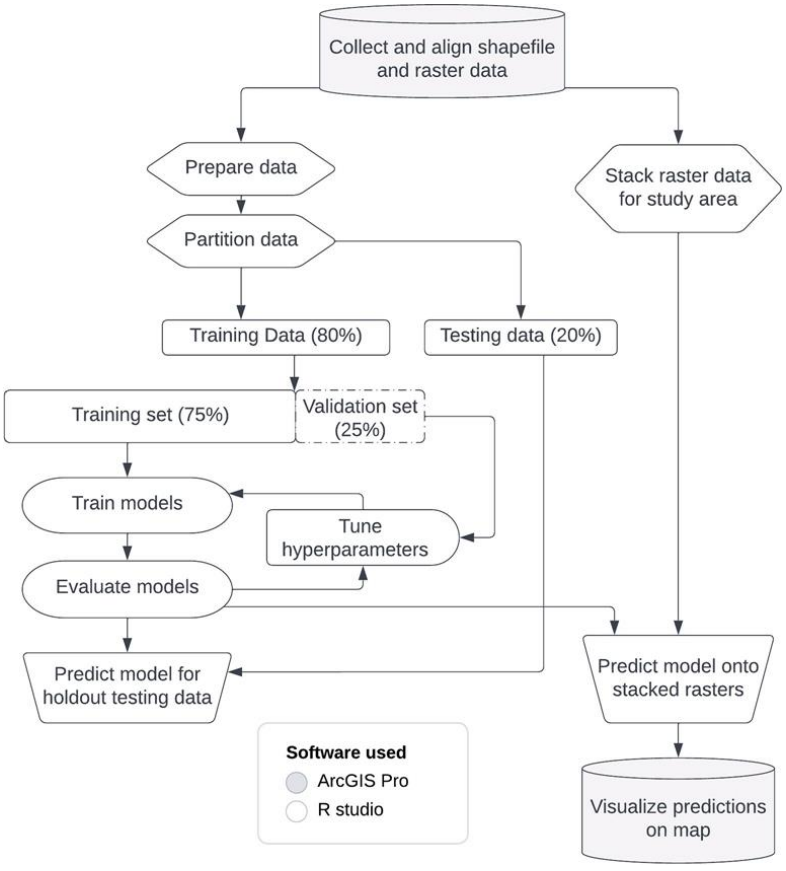

Figure 11 Main steps in the hybrid geographical information systems (GIS) and machine learning workflow. Adapted from Object Research Systems, 2023.

3.2.5 Spatial explanatory variables

The current study builds on the results of a 2019 USGS study identifying factors associated with TCP contamination in groundwater. We also consider a set of land use source data from the years (1945, 1960, 1975, 1990, 2005) that delineates specific agricultural land use classifications (Harter et al., 2017). Mass balance estimates are not used as an explanatory variable in the models because the initial concentration of applied TCP is not based on crop or area-specific inputs but rather considers averages of all crop inputs statewide. The data used in the current study is all open source (Table 6) to understand the predictive power of these publicly available datasets. The shapefile and raster layers were projected using an equal area Albers projection with a North American Datum (NAD) of 1983.

3.2.5.1 Nitrate and dissolved oxygen concentration - raster data

Nitrate concentration and TCP concentration are significantly related (Burow et al., 2019). Spatial data for nitrate concentration was obtained from the USGS data release for predicting nitrate in the Central Valley Aquifer Region. Nitrate values were predicted using a Boosted Regression Trees (BRT) model at two different depths, one related to private wells (180 feet or 54.9 m) and another related to public drinking water wells (400 feet or 123 m). The nitrate point data, on which the BRT model was constructed, come from the University of California at Davis (UC Davis) and the U.S. Geological Survey (USGS) (Ransom et al., 2017a).

Since California groundwater wells with the highest TCP concentration tend to be in oxic wells, this study uses dissolved oxygen (DO) concentration as an explanatory layer (Burow et al., 2019). DO raster grids were constructed by the USGS where raster values are expressed as probabilities that groundwater in a particular area has DO concentrations less than certain threshold values (2 mg/L and 0.5 mg/L); the higher the probabilities, the more likely that a well is anoxic (Rosecrans et al., 2018). Depths for domestic and public supply wells used for this study are at 30 m and 100 m respectively.

3.2.5.2 Land use, irrigation, and precipitation - raster data

The agricultural land use surrounding each well was calculated using California Augmented Multisource Landcover (CAML) maps, which categorize agricultural land use for the following years: 1945, 1960, 1975, 1990, and 2005 (Harter et al., 2017). The twelve specific land uses categorized by the CAML maps include (1) urban; (2) native vegetation; (3) pasture; (4) citrus and subtropical; (5) deciduous fruit and nuts; (6) field crops; (7) corn, sorghum, and sudangrass; (8) grain; (9) alfalfa; (10) truck, nursery, and berry; (11) rice; and (12) vineyards (SM Table S6). CAML maps were created and used to analyze nitrate loading in groundwater as presented in a 2017 technical report for the Fertilizer Research Education Program (Harter et al., 2017). As TCP was applied from the 1940s to the 1980s, these older maps offer a more accurate description of land use patterns during fumigant application and therefore may show a stronger correlation than current land use maps to TCP contamination in groundwater.

CAML maps modeling the nitrogen levels in irrigation water were also used for 1945, 1960, 1975, 1990, and 2005. Since these raster layers were originally created for a nitrate study the map units are in kg Nitrate/hectare/year (kg N/ha/yr) and account for pumped ground- water application contributing to nitrate loading. Nitrate loading from

irrigation serves as a proxy for historical irrigation estimates which would have influenced TCP migration in the subsurface.

Parameter-elevation Regressions on Independent Slopes Model (PRISM) was developed in 1991 to estimate precipitation. PRISM uses point data from multiple monitoring networks and climactically aided interpolation (CAI) to model precipitation (PRISM Climate Group, 2021). This study uses mean annual precipitation (mm/year) for 1945, 1960, 1975, 1990, and 2005. The raster grid has a resolution of 4 km.

Table 6 Data source and information for explanatory variables

Explanatory Variable	Unit	Layer type	Variable Type	Data Source
Dissolved oxygen	mg/L	1000-meter resolution raster	Numerical	USGS Probability distribution grids of dissolved oxygen (Rosecrans et al., 2018) https://www.sciencebase-.gov/catalog/item/57f433c3e4b0bc0bec033fc9?community=USGS+California+Water+Science+Center
Groundwater age	year	Polygon	Numerical	Estimation of tritium-helium age dating of groundwater sampled under the GAMA Program, by Lawrence Livermore National Laboratory (Visser et al., 2014) https://waterboards.maps.arcgis.com/home/item. html?id=69fa92fc0-2e946b29c4911af13f50b1a
Irrigation	(kg N/ha/yr)	50-meter resolution raster	Numerical	CAML 1945 - 2005 (Harter et al., 2017) UC Davis Center for Watershed Science: http://ucd-cws.github.io-/nitrates/maps/
Land Use	(-)	50-meter resolution raster	Categorical	CAML 1945 - 2005 (Harter et al., 2017) UC Davis Center for Watershed Science: http://ucdcws.git-hub.io/nitrates/maps/
Nitrate concentration	mg/L	1000-meter resolution raster	Numerical	USGS Groundwater nitrate data. (Ransom et al., 2017b) https://-www.sciencebase.gov/catalog/item/58c1d920e4b014cc3a3d3b63
Precipitation	mm/year	4-kilomoeter resolution raster	Numerical	PRISM Climate Group: Northwest Alliance for Computational Science and Engineering 1945-2005 (PRISM, 2021) https://prism.oregonstate.edu/
Soil drainage class	(-)	30-meter resolution raster	Categorical	USDA SSURGO - Soil drainage class. USDA NRCS, Esri https://www.arcgis.com/home/item.html?id=55d0c2d32c234ce497cd30dc9bc06729
Soil hydrologic group	(-)	30-meter resolution raster	Categorical	USDA SSURGO - Soil hydrologic group. USDA NRCS, Esri https://www.arcgis.com/home/item.html?id=be2124509b064754875b8f0d6176cc4c

3.2.5.3 Soils - raster data

Since infiltration and loading of TCP into groundwater may be affected by the hydrologic and drainage class of soil (Burow et al., 2019), data from the USDA Soil Survey Geographic Database (SSURGO) is included in this analysis (USDA, 2021). These 30-m resolution raster layers were produced by the U.S. Department of Agriculture Natural Resources Conservation Service (NRCS). Hydrologic Soil Groups (HSG) fall into one of eight categories based on runoff versus infiltration po- tential (SM Table S7) (Mockus, 1964; USDA, 2019). The drainage class of soils, or their relative ability to retain or drain water, is also considered an explanatory factor. SSURGO divides drainage into eight different classes: excessively drained (0); somewhat excessively drained (1); well drained (2); moderately well drained (3); somewhat poorly drained (4); poorly drained (5); very poorly drained (6); and subaqueous soils (7) (USDA, 2017) (SM Table S8).

3.2.5.4 Groundwater age - raster data

Groundwater age data is from GAMA gathered through a program conducted by the Lawrence Livermore National Laboratory (Visser et al., 2014). The classification of groundwater age is based on the relative concentration of radioactive tritium (3H) to helium-3 (3He). Modern-age groundwater (recharged in 1953 or later) has previously been associated with higher concentrations of TCP in groundwater wells (Burow et al., 2019)

3.2.5.5 Disadvantaged communities' data

As other agricultural groundwater contaminations like nitrates are found disproportionately in disadvantaged communities (DACs) (Tariqi and Naughton, 2021), we used the California Office of Environmental Health Hazard Assessment (OEHHA) and California Environmental Protection Agency (CalEPA) CalEnviroScreen 4.0 geodatabase to determine if areas with high-modeled TCP contamination are also more likely to occur in underserved regions (OEHHA, 2021). The CalEPA tool delineates DAC locations and boundaries based on socioeconomics, public health, and combined environmental pressures. Communities that rank in the top 25% of combined evaluation categories are considered disadvantaged

3.2.5.6 Shapefile boundary layers for California and the Central Valley aquifer

The boundary of the Central Valley aquifer was obtained by con- verting the land use raster data to a shapefile and then dissolving all internal boundaries. The explanatory layers and TCP target variable point data layer described in the previous sections were compiled in ArcGIS Pro and clipped by the boundary. This boundary was selected to maximize available land-use data. California state and county boundary layers were obtained from the California Department of Technology Open Data Portal (CDT, 2019).

3.2.6 Spatial machine learning models

A variety of modeling approaches have been used to predict nitrate and arsenic groundwater concentration, including Multiple Linear Regression (MLR) and Artificial Neural Networks (ANN) (Nolan et al., 2015). However, not all methods can accommodate both categorical and continuous measurement scales as easily as decision

trees can (Georganos et al., 2021). Three different types of regression decision trees were used to predict TCP groundwater concentration in California's Central Valley: Classification and Regression Trees (CART), Random Forest (RF), and Boosted Regression Trees (BRT). Single decision tree models, like CART, can overfit the training dataset. However, ensemble methods (RF and BRT) average results from hundreds of differently structured trees and therefore generally show higher pre- dictive accuracies and lower variances (Breiman, 2001). Two common ensemble methods are bagging (for RF models) and boosting (for BRT models) (Breiman, 2001). The bagging method trains multiple decision trees in parallel, with each tree trained on a different subset of the data. On the other hand, the boosting method is sequential; each tree learns from the preceding tree.

3.2.6.1 Classification and Regression Trees

Classification and Regression Trees (CART) are commonly used decision tree algorithms developed by Leo Breiman (Belgiu and Dra˘gut¸, 2016; Breiman, 2001). CART models are used for categorical and regressive predictive modeling. CART is based on a decision tree structure that begins with the entire set of training data at the root node. Each split of the tree creates non-terminal daughter nodes until terminating at leaf nodes, which are a unique prediction of the target variable (Brei- man, 2001; Knoll et al., 2019). The CART algorithm determines the variables used for splitting, where split points are located, and the shape of the tree (Hastie et al., 2017). Single large decision trees have a tendency to overfit the data; the CART algorithm is advantageous over more basic decision tree models because it "prunes" large trees to create a smaller tree with a lower error rate (Hastie et al., 2017). Because the CART model prediction outcome is based on the results from a single pruned tree, its predictive performance is sometimes lower than ensemble methods, which are based on the outcome of hundreds of trees. The CART approach lays the foundation for ensemble methods such as RF and BRT and is therefore evaluated in the present study as a basic model for comparison.

3.2.6.2 Random Forest

Random Forest (RF) is a machine learning algorithm based on mul- tiple decision trees which are considered collectively and, as a result, the technique is sometimes referred to as an ensemble learning method (Breiman, 2001). Trees are built from random selection variables using training data. The approach can be used to predict categorical or continuous data from many predictor variables. Since RF relies on averaging the results from multiple randomly constructed CARTs to make a prediction, it generally shows greater accuracy and less over- fitting than models based on single CART trees (Naghibi et al., 2016). In the process of RF regression, a set number (B) of regression trees (Tb) are grown, and the outputs are then averaged. The regression prediction for a new data point (x) is defined by the following equation (Hastie et al., 2017).

$$\hat{f}\ \frac{B}{rf}\ (x) = \frac{1}{B}\sum_{b=1}^{B} Tb(x)$$

Each tree is trained on a random subset of 75% of the training data. Then, the excluded one-quarter of the data (known as "out-of-bag" data) is run back through the tree. Out-of-bag errors indicate how well each tree can predict the excluded features.

3.2.6.3 Boosted regression trees (BRT)

Like RF, a BRT model uses the results from hundreds of multiple decision trees. Unlike RF, BRT is a sequentially constructed model that considers the residuals of the previous trees when constructing a new tree. If input data is successfully modeled in a tree, that data then has a higher chance of being included in the subsequent tree thereby "boosting" the model (Hastie et al., 2017). BRT also deviates from the RF model in which inputs have an equal and random probability of being included in any one tree and are not dependent on the outcomes of previously constructed trees. BRT hyperparameters include the tree complexity, to determine the number of splits in a tree, the learning rate, which sets how much the outcome of one tree can influence how a future tree is assembled, and the minimum number of observations at the leaves or terminal nodes of the trees (Elith et al., 2008; Mosavi et al., 2020).

3.2.7 Model construction, testing, and evaluation

After joining buffered well-point data with explanatory variables into a data frame, the data was split into a training set (80%, n = 10,652) and a testing set (20%, n = 2,662) using a data partitioning function from the caret package (Kuhn et al., 2018). The 'set.seed' function in R was used to make sure that the same random split of data was used to train each of the different models (R Core Team, 2020). To reduce overfitting and bias, we used the caret package 'trainControl' function to conduct a three-times repeated 10-fold cross-validation on the training dataset using all twenty input variables (Table 1) (Kuhn et al., 2018). To create the cross-validation folds, the training data was repeatedly and randomly split into 10 smaller sets with 25% of the training data held out as a validation test set (Figure 11). The final hyperparameters that we selected were based on the lowest RMSE value from the cross-validated training runs. The range of tuning parameters used to adjust the models during the tuning phase and the final hyperparameters used to construct the models are in Table 7.

Table 7 Hyperparameter and ranges applied during cross-validation tuning. Hyperparameters were selected based on the lowest root mean square (RMSE) value in cross-validated training runs.

Model	Parameter	Description	Range of parameter tuning values	Parameter values with lowest RMSE score
Classification and Regression Trees (CART)	max depth	Tree size	2:20, by 1	6
Random Forest (RF)	mtry	Number of variables to randomly sample at each split point of a tree	2:20, by 2	16
Gradient Boosted Regression (GBR)	Interaction depth	Number of split points in a tree	8:16, by 2	12
	n.trees	Number of trees in the forest	500:3000, by 500	3000
	shrinkage	Learning rate	0.002:0.02; by 0.002	0.02

Since tree-based models are known to underpredict high concentrations and overpredict low concentrations, we applied empirical dis- distribution matching (EDM) bias correction. EDM couples values from the cumulative distribution functions of both the observed and predicted TCP values to correct systemic bias (Belitz and Stackelberg, 2021) and has been previously used in tree-based decision models to predict groundwater nitrate levels (Ransom et al., 2022) Finally, the three models (with and without bias correction) were evaluated against one another for overall predictive performance using caret functions for common metrics to compare machine learning algorithms: mean absolute error (MAE), root mean squared error (RMSE), and the coefficient of determination (R^2) (Kuhn et al., 2018; Knoll et al., 2019; Nolan et al., 2015). For the model with the lowest MAE and RMSE values and highest R^2 value, a variable importance plot was constructed to show how important each variable is in predicting TCP levels (Figure 5). Additionally, partial dependence plots helped us to understand the relationship between a single variable and TCP predictions (SM Figure S4).

3.3 Results and discussion

California's Central Valley has some of the highest numbers of drinking water violations from a variety of contaminants in the state (Balazs, 2010). The proportion of Central Valley wells that test above the MCL for TCP is over 10% higher than the California average (Love, 2019). TCP was a trace impurity in 1,2-DCP fumigant formulations, and as the actual concentration of TCP may have been as high as 7% and as low as 0.17%, a high and low estimate is provided in the mass balance model (see Table 8 and SM Figure S2) (Oki and Giambelluca, 1987; Zebarth et al., 1998). The estimated mass of TCP accumulated over 30 years, accounting for diffusive loss to surroundings, is 110,000–4,300,000 kg of TCP.

This balance focuses on diffusive loss as TCP's Koc is low, 2–2.5. As such, sorption to soil organic matter is relatively low and unlikely to substantially hinder TCP transport to groundwater (Mital, 2014). Moreover, the machine learning model we use shows that hydrologic soil type and drainage characteristics are relatively unimportant predictors of TCP in groundwater (Figure 5). Finally, although fumigant residues have been detected in plants since fumigants are generally applied before crops are planted, plant uptake is considered negligible and not considered by this model.

Table 8 Mass balance results of using 7% and 0.17% by mass of 1,2,3-trichloropropane (TCP) in fumigant formulations from estimates in Oki et al. (1987) and Zebarth et al. (1998) respectively.

Percent TCP by mass in fumigant formulation	**7%**	**0.17%**
Estimated mass accumulated over 30 years accounting for diffusive loss to surroundings (kg)	4,300,000	110,000
Area applied (hectares)	16,000	16,000
Mass loss per unit area (kg/hectare)	270	7

3.3.1 Decision tree models

3.3.2 Summary statistics for TCP well data used for model training

The TCP concentration for the well point data (n = 13,314) used to train the models ranged from 0.0025 to 60 µg/L with a median con- centration of 0.0025 µg/L and a mean concentration of 0.24 µg/L. Of the different well categories, "municipal" were the most abundant (47%); followed by "monitoring" (43%); "other water supply" (8%); and

"domestic" (2%). Monitoring wells had the highest mean concentration of TCP at 0.44 µg/L followed by domestic (0.097 µg/L), municipal (0.090 µg/L), and other water supply (0.011 µg/L). Well depths ranged from 8.2 to 2100 feet with a median and mean depth of 90 feet and 180 feet respectively (SM Table S4).

3.3.3 Buffer zone comparison

Each of the tested decision tree models is based on a set of explanatory variables surrounding groundwater well points. For each model, three different buffer zones (500-m, 1000-m, and 1500-m) were tested around those well points and evaluated for predictive performance for the testing data using MAE, RMSE, and R^2 metrics. Initial modeling results found little difference in model performance between buffer sizes. Slightly higher R^2 values and lower RMSE and MAE values occurred in a 1000-m buffer zone (SM Figure S3). Using a 500-m buffer zone produces the lowest R^2 value except for the single tree CART model in which the 1500-m buffer yields the poorest performance.

3.3.4 Predicted performance

The models' predictive performance results are presented in SM Table S8 for both training and testing data. Of the models tested, the RF model produces the best predictions with the highest mean R^2 value of 0.44 and the lowest MAE (0.43) and RMSE (0.72) values. As expected, the single tree CART model is the least accurate with an R^2 of 0.020 and higher MAE and RMSE values than either of the RF models. Although the BRT models have performed better than the RF model for nitrate prediction in the Central Valley (Ransom et al., 2017b), for TCP the BRT R^2 value (0.41) is slightly lower than that of the RF model (0.44) (SM Table S8).

The observed TCP concentration versus the predicted TCP concentration for the training and hold-out testing data for all models is plotted in Figure 12. Ideally, the plotted points should be close to the regression line and equally scattered above and below it, however, actual results are dispersed for the testing data sets. While not surprising considering the range of TCP concentration values (0.0025–60 µg/L), increasing variance with larger concentration limits the model's ability to make ac- curate predictions and future models may consider a narrower range of TCP concentrations to train the model.

The R^2 Random Forest model performance result for the training data is similar to the results from studies using similar decision tree methods to predict concentrations of other agricultural contaminants such as nitrate (Knoll et al., 2019; Ling et al., 2022; Ransom et al., 2017a). The predictive performance values for the training data set show significantly better results than for the test data for all three models, but the largest difference between training and testing predictive performance is the BRT model, indicating an overfit to training data slightly more than the other tested models.

3.3.5 Variable importance tables and partial dependence plots

The performance of explanatory variables (Figure 13) shows how well each variable performs in splitting the decision trees to predict TCP concentration. For the RF model, which had a higher predictive performance than the CART or BRT models, the most influential predictors categories are annual precipitation amount from 2005, 1990, 1960, and 1975; two groundwater redox variables indicating the probability of dissolved

oxygen levels being below 2 mg/L and 0.5 mg/L; and nitrate as estimated from concentration at 180 feet depth. The finding agrees with an earlier study that found precipitation and redox state to be the factors most associated with detecting volatile organic compounds in domestic wells (Rowe et al., 2007).

Partial dependence plots for predictor variables allowed us to explore the individual relationships between a variable and its influence on the model (SM Figure S4). The importance of precipitation, the most influential category, shows that the highest concentrations of TCP are associated with the lowest rainfall levels for all years. The two top predictors, precipitation during 2005 and 1990, are for years after TCP would have ceased to be applied. So, it may follow that higher rainfall could have diluted wells already contaminated with TCP, with higher TCP levels in wells with lower recharge rates. Additionally, the highest modeled TCP concentrations are in the southern area of the Central Valley where precipitation rates are relatively low but with large swaths of land use developed for orchards and row crops. Precipitation during 1960 and 1975 shows a different trend, with an unsymmetric V-shaped curve. For these years, although the highest TCP levels are still associated with the lowest levels of rainfall, TCP levels dip and then show an upward trend with rising precipitation amounts. TCP was still being actively applied during 1960–1975 and therefore the connection be- tween high precipitation levels and high TCP concentration may be because high levels of precipitation may have led to an increased chance that TCP leached from soil fractions into the water table and may have been the case during years when TCP was actively applied and when the concentration of TCP in the soil would have been the highest (Lewan et al., 2009; McGrath et al., 2010; Ney, 1990). This tendency may have been especially true in well-drained soils, with high infiltration rates (Bailey et al., 1974). The upward trend may also be related to observed training points with very high (>20 μg/L) TCP levels in urban areas near Stockton and Sacramento, California. Contamination in these wells may be due to the past industrial use of TCP or because they are in the northern sections of the Central Valley, where precipitation rates are higher. The multi-faceted relationship between TCP levels and precipitation may also be confounded by the presence of undissolved TCP in the unsaturated zone where water tables rise during precipitation events and groundwater may become periodically recharged with TCP.

Partial dependence plots for the second highest importance category, redox state, show a U-shaped trend with high TCP levels in groundwater with a high probability of being oxic and anoxic with the lowest TCP concentrations at mid-level probabilities that dissolved oxygen levels are below a 2 mg/L or a 0.5 mg/L threshold. This finding partially agrees with previous research which has shown that TCP is found at higher concentrations in oxic groundwater due to the prevention of the chemical transformation of TCP which may occur in anoxic conditions (Burow et al., 2019). Higher concentrations of TCP in anoxic ground- water may be the result of the lateral migration of TCP towards the Central Valley central axis trough region which is more associated with anoxic groundwater (Ransom et al., 2017a; Rosecrans et al., 2018).

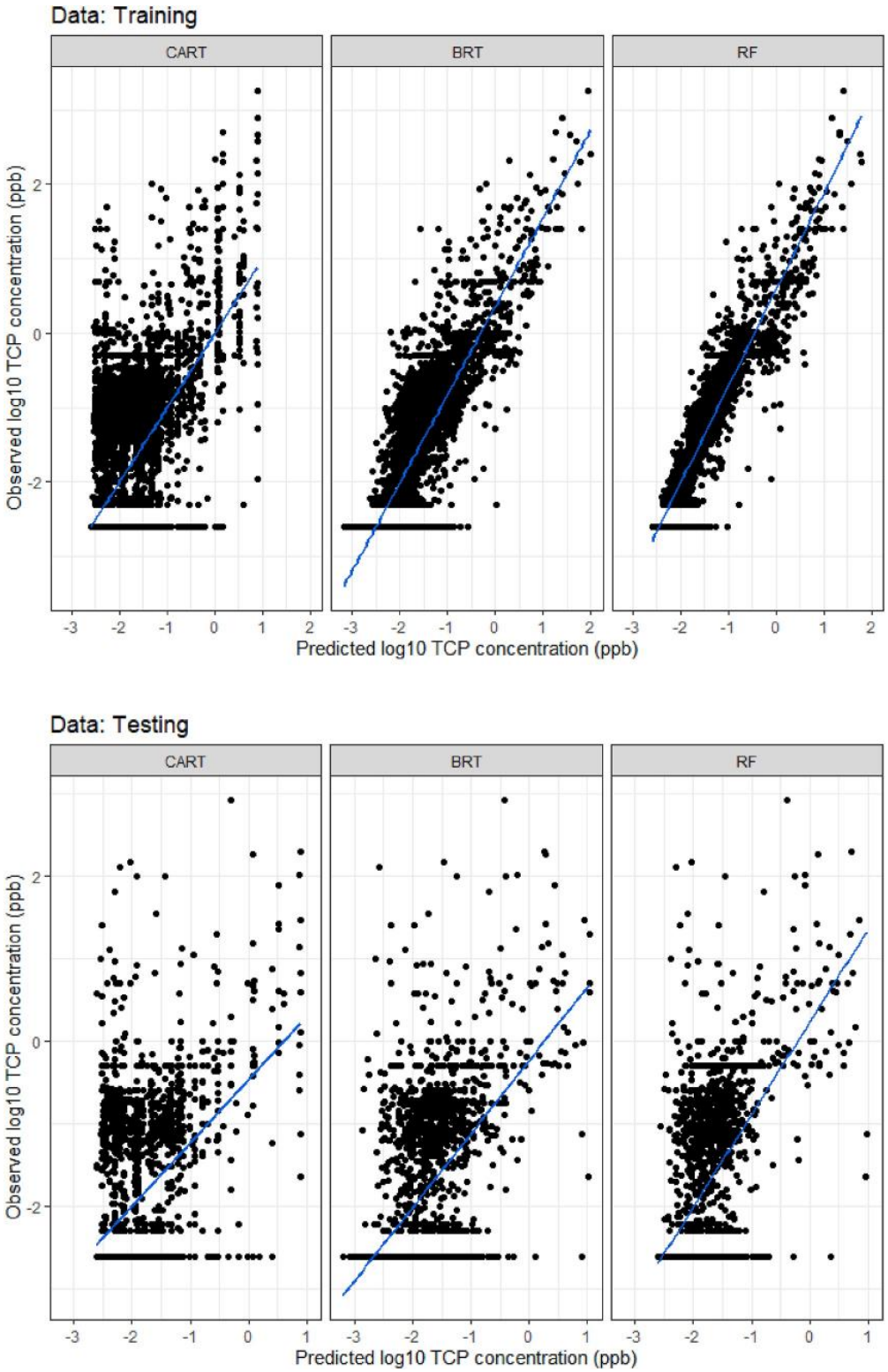

Figure 12 Predicted vs. observed 1,2,3-trichloropropane (TCP) concentrations for training data (above) and test data (below) for all models based on a 1000-m circular buffer zone.

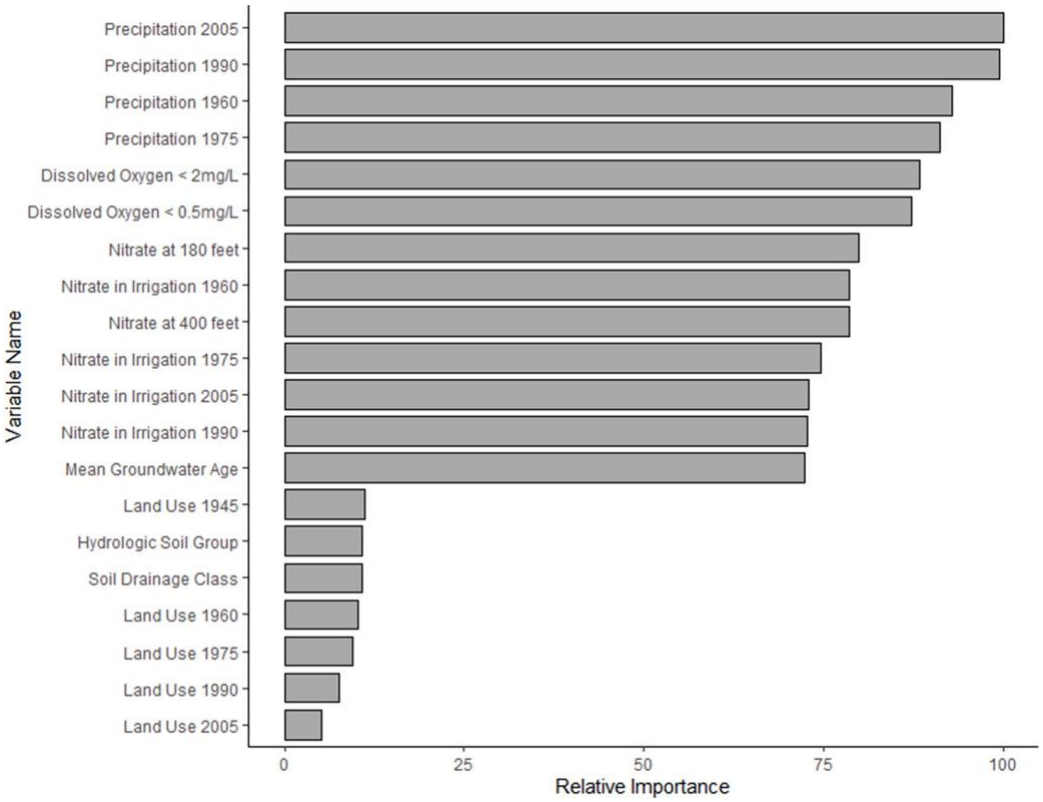

Figure 13 Explanatory variables and their relative importance for prediction of 1,2,3-trichloropropane (TCP) concentration in groundwater using the Random Forest (RF) model. Partial dependence plots can be found in SM Table S9.

The third influential prediction category, nitrate levels, underscores that the principal source of TCP in CVAR groundwater is related to the agricultural use of fumigants as opposed to TCP's use as an industrial solvent (Burow et al., 2019). Partial dependence plots show that higher TCP levels are positively associated with higher levels of the co-contaminant nitrate. The plots also show a spike in concentration at very low levels which may be the result of industrial uses of TCP as a lubricant and degreaser (Burow et al., 2019).

Less influential factors include irrigation, groundwater age, and land use classes. Irrigation may have had less of an influence as application instructions for the fumigant in which TCP was contained advised growers to leave treated soil undisturbed for at least 7–14 days, specifically noting that wet soil disturbs the diffusion process (USEPA, 1973). Land use may be less influential than expected because agricultural land use layers used were for discrete years with a 15-year gap between years (1945, 1960, 1974, 1990, 2005) and therefore may not reflect the actual crop types in a particular area during the years when TCP would have been applied. Furthermore, the decision to use fumigants that would have contained TCP would have been influenced by the affordability and availability of the fumigants, and the differences in TCP concentration from batch to batch.

3.3.6 Median TCP concentration by agricultural land use

Although the relative importance of specific agricultural land designation by crop type is low, we compared specific crop types directly to TCP levels in surrounding wells. The land use in a 1000-m buffer zone around well points was used to calculate the median TCP concentration in µg/L in groundwater under particular crop types (SM Table S8 and Figure S2). We found that in the Central Valley, regardless of year, the highest median TCP concentration (0.03 µg/L) occurs in groundwater below vineyards compared to other land use designations. The second highest concentrations are in field crops, followed by alfalfa, deciduous fruit and nut, grain, corn, sorghum, sudangrass, and native vegetation. The groundwater beneath citrus and subtropical, rice, truck nursery and berry, and urban areas have zero median TCP concentration for all years.

3.3.7 Spatial prediction of TCP groundwater concentrations

Our models were largely underpredicting TCP concentrations, especially at the lower end of the spectrum. Applying the EDM bias correction resulted in adjustments that increased underpredicted low values, reduced overpredicted high values, and increased R^2 values for the hold-out testing data (Figure 14, SM Table S8).

The spatial distribution of EDM bias-corrected TCP predictions for Central Valley groundwater was mapped to a 50 × 50 m raster grid for all models (Figure 15). The RF prediction map, which showed the highest performance in comparison to CART and BRT, indicates that the 0.1–0.2 µg/L TCP contamination range makes up the largest total percentage (56%) of the Central Valley Aquifer study region groundwater. The highest TCP concentration range (0.4–0.86 µg/L), as predicted by the RF model, occurs at the lowest total area of only 1% or 586 km2 (SM Table S9) and occurs predominately in the southern San Joaquin Valley region of the CVAR. Approximately 48% of the CVAR includes disadvantaged communities (DACS) as defined by the OEHHA (OEHHA, 2021). The highest modeled TCP groundwater concentration range oc- curs predominantly in DACS (73%) (SM Table S10).

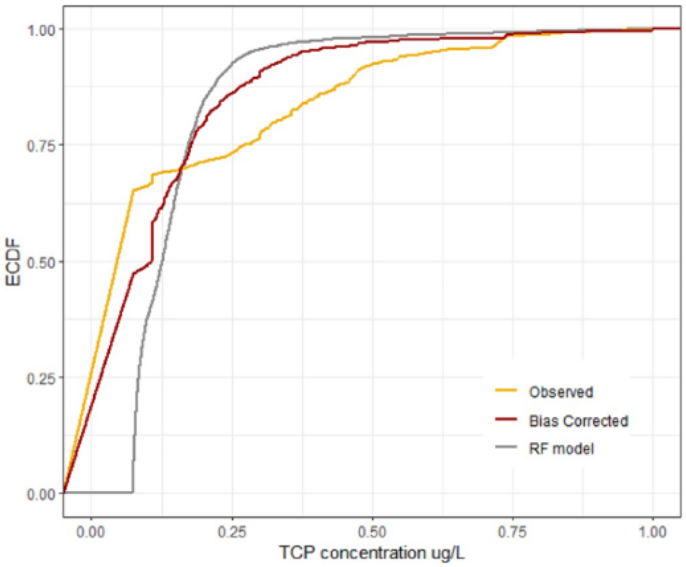

Figure 14 Empirical cumulative distribution function (ECDF) for hold-out data, observed, Random Forest (RF), predicted, and empirical distribution matching (EDM) bias-corrected.

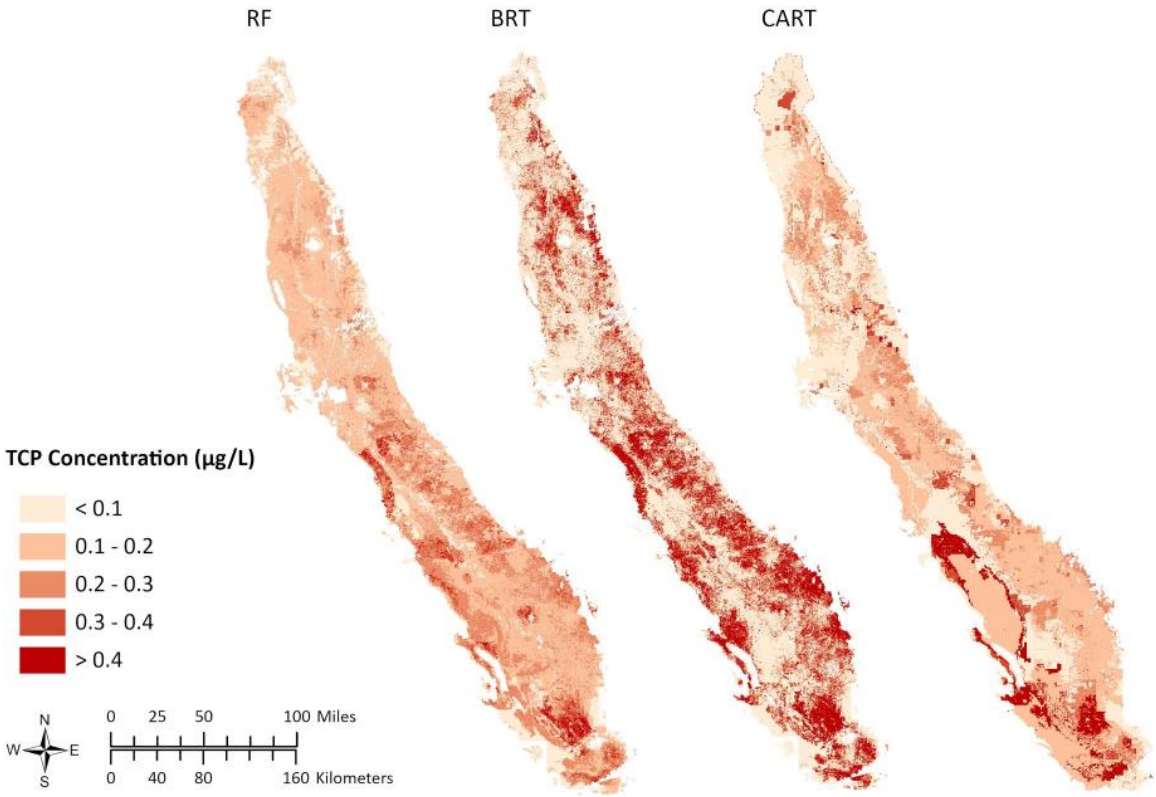

Figure 15 Predicted groundwater 1,2,3-trichloropropane (TCP) concentrations in the Central Valley aquifer using Random Forest (RF), Boosted Regression Tree (BRT), and CART models mapped to 50×50 meters. White areas are due to missing data for one or more explanatory variable.

3.4 Conclusions

A mass balance using data from historical PUR documents indicates that during the approximately 30 years that TCP was applied to agricultural lands, 110,000–4,300,000 kg of TCP may have accumulated in the subsurface and leached into California groundwater. This TCP groundwater loading estimate is based on two contributing pesticides: Telone and D-D mix. However, since TCP was an impurity retained after 1,2-DCP was manufactured, other fumigants may have also contained TCP and their exclusion may have led to an underestimate of TCP loading. Additionally, future efforts may include irrigation schedules and multiple fumigant application methods such as tarping with plastic following fumigant application.

This study provides the first-ever machine learning model for a volatile contaminant in groundwater. It is an important initial analysis and suggests a model for predicting amounts of TCP in the subsurface that can be applied to agricultural regions globally. Future studies may take advantage of several refinements. The models in the present study are trained with wells monitored for TCP using 1000-m circular buffers, however, future TCP spatial modeling may improve outcomes by using different buffer shapes and by integrating groundwater flow models to capture horizontal migration of TCP in the subsurface. While this study includes dissolved oxygen as an indicator of the redox state of ground- water, by including a full series of redox indicators, such as

manganese and iron, a clearer picture of the importance of the redox state in predicting TCP in affected wells may result. A comparison of crop type and median TCP concentration in 1000-m buffer zones surrounding monitored wells using five historical agricultural land use maps between 1945 and 2005 shows that vineyards have the highest median TCP concentration for all years in the study region. However, crop type was the least important explanatory predictor for TCP concentration with the RF model. Future models may therefore consider using land use maps with fewer agricultural categories, with the added benefit of reducing the computational cost of training the models.

The GIS-based machine learning approach used in this study allows for the prediction of TCP concentration from spatially mapped environmental explanatory variables. According to R^2 values, the three models were ordered in terms of predictive performance as RF > BRT >CART. Bagged tree models constructed in parallel slightly outperform boosted tree models constructed sequentially. The single tree CART model has a substantially lower performance than either boosted or bagged multitree models. The EDM bias corrected RF model has an R^2 value of 0.43 using the testing data set (20% of the full data set). Using the RF model, the most important predictors for the spatial occurrence of TCP in groundwater are precipitation, dissolved oxygen levels, and nitrate concentration. The type of prediction maps produced by this analysis could be used by water districts and domestic well owners in areas not monitored for TCP.

With water insecurity increasing in many areas of the world, well- managed and monitored groundwater supplies are of growing importance. This research supports UN SDG goals 3 and 6, reducing illness from pollution and access to safe and affordable drinking water (UNSDG, 2015). Models have shown that TCP is an animal carcinogen, and it is a suspected human carcinogen. The Central Valley of California contains numerous rural communities with private wells, small water systems, and limited budgets. Many of these communities are classified as disadvantaged communities, and since TCP treatment and monitoring are expensive, predictive models may alleviate some of the expense by helping to target limited resources toward drinking water sources most likely to be contaminated. Data used to train and test the models and R code are available publicly and can be found at: https://github.com/hopehauptman/TCP_MachineLearningModel.

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3.5 Chapter 3 References

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Chapter 4. Evaluation of Point-of-use Treatments and Biochar to Reduce 1,2,3-Trichloropropane (TCP) Contamination in Drinking Water

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Abstract

From the 1940s to the 1980s, 1,2,3-trichloropropane (TCP) was widely present as an impurity in soil fumigants to eliminate plant parasitic nematodes. TCP also saw wide usage as a degreaser and solvent in industrial processes. In rural agricultural regions with a history of fumigant use, TCP is a common pollutant in groundwater. As a potent suspected carcinogen (California MCL 5 ng/L), TCP poses a risk to communities reliant on domestic wells. Lacking the populations needed for more centralized water treatment facilities, these communities often use point-of-use (POU) treatment technologies or buy bottled water. In this study, we tested commercially available water pitchers equipped with carbon filters for point-of-use TCP treatment efficacy. As a less costly carbon alternative, we also tested low-cost, locally sourced biochar made from almond shells. Biochar could serve as a sustainable alternative to the current coconut and coal-based carbon feedstocks. Pitcher point-of-use (P-POU) filters removed at or above 98% of TCP in tap water derived from untreated groundwater during their lifetime of use. In our batch studies, almond biochar did absorb TCP at a lower efficiency than commercially available granulated carbon. Ultimately, the study's findings could assist affected communities and households in identifying efficient and cost-effective treatment technologies at the domestic well and household levels.

4.1 Introduction

In 2010, the United Nations General Assembly passed a resolution recognizing the Human Right to Water and Sanitation (United Nations, 2010). However, in 2020 approximately 1 in 4 people lacked safe drinking water access in their homes (UNICEF, 2021). Rural communities with limited resources and small water systems are more likely to have unsafe drinking water (Pace et al., 2022). These communities often lack access to safe and affordable alternatives (London et al., 2018). Moreover, rural communities located in or near agricultural areas face additional challenges, such as water contamination from pesticides and agricultural amendments Ravenscroft et al., 2022).

The San Joaquin Valley (SJV) in California, USA is a prime example of this issue. The SJV's eight counties are home to some of California's lowest-income communities and the highest number of drinking water violations (Balzas et al., 2010). One of the most persistent chemical contaminants found in SJV's groundwater is 1,2,3-trichloropropane (TCP), a suspected human carcinogen (Hauptman and Naughton, 2021).

In California, the maximum contaminant level (MCL) of TCP in drinking water has been set at a low 5 ng/L due to the potential risk of cancer (SWRCB, 2017). In carcinogenic dose-response studies with rodents, the oral slope factor which measures the "incremental lifetime risk of cancer by oral intake of the chemical" for TCP is 3×10^{1} per

mg/kg-day which is three orders of magnitude greater than the oral slope factor for similar chlorinated organic contaminants such as TCE (4.6×10^{-2} per mg/kg-day) (USEPA IRIS, 2009). About 8% of domestic wells in California have levels of TCP above the MCL compared to 5% of municipal wells (Burrow et al., 2019).

Water utilities use granular activated carbon (GAC) as the best available treatment technology to remove TCP and achieve low MCLs (Hauptman and Naughton, 2021). Carbon has been utilized for centuries to eliminate impurities and improve the taste and odor of drinking water (NRC, 1980). Modern carbon filters are composed of finely ground particles of wood, coal, or nutshells that have been treated chemically or heated to create surfaces with high sorption capacity (Bansode et al., 2003). However, water consumers lack evidence-based information on the effectiveness of sustainable carbon sources and point-of-use treatments to remove TCP. To address this issue, we conducted a batch isotherm analysis to determine the adsorptive capacity of biochar made from almond shells.

Biochar is similar to GAC but can be produced at significantly lower costs and with fewer energy inputs (Huggins et al., 2016). Multiple types of biochar were found to remove both organic and inorganic contaminants from water in a recent review (Palansooriya et al., 2020). Previous studies have shown that biochar derived from agricultural byproducts such as pecan and almond shells could remove volatile contaminants like benzene and chloroform, but not TCP (Bansode et al., 2003). Although shell waste has been used for cogeneration facilities in the past, this practice is being phased out in California due to strict air quality regulations, resulting in increased shell mass in the waste stream. As approximately 80% of the world's almonds are grown in California (Kendall et al., 2015), using almond shell waste as a source of carbon to remove pesticide contaminants such as TCP from groundwater could be a more locally sustainable solution than importing coconut or coal-based carbon GAC feedstocks (Babcock et al., 2018).

In addition to the lack of knowledge about the utility of using local nutshell-based biochar, there is a lack of knowledge concerning the efficacy of point-of-use (POU) filters in reducing TCP levels in drinking water. Tap water consumers in California's Central Valley are concerned about the safety of their drinking water supply, specifically about the potential presence of pesticide contaminants, which is a grave concern for domestic well owners (Fernandez-Bou et al., 2021). Since the Safe Drinking Water Act (SDWA) does not cover private wells, domestic well users are responsible for both arranging to monitor and for paying the treatment costs (SDWA, 1996). Moreover, a 2019 study by the USGS concluded that shallow private domestic wells have significantly higher TCP concentrations than public supply wells due to their proximity to agricultural fields and relatively shallow depths (Burow et al., 2019). Using low-cost POU filters may empower domestic well users who are at an elevated risk for TCP exposure by allowing households to play a direct role in the safety of their water supply while reducing the reliance on costly water bottled in plastic (Sobsey et al., 2008).

There are several studies documented in the literature that used carbon-based POU filters for the removal of metals such as lead and arsenic and trace organic compounds (Mulhern et al., 2020; Gulson et al., 1997; Anumol et al., 2015; Doré et al., 2021). A study by Brown et al. (2017), notes that POU filters may be effective to mitigate health risks from exposure to contaminants and that this may be especially true for

substances not treated by typical water treatment approaches (Brown et al., 2017). Both the NSF (National Sanitation Foundation) International and ANSI (American National Standards Institute) certify some POU filters in their ability to reduce volatile organic contaminants with an NSF/ANSI 53 certification, but none specifically test for TCP removal.

The overall goal of this research is to conduct a treatment analysis for TCP in drinking water supplies. Specific objectives include (1) evaluating the efficiency of pitcher point-of-use (P-POU) treatments for their ability to lower TCP levels and (2) evaluating almond shell-derived biochar for TCP sorption. This study's results will inform communities, water utilities, and almond producers with updated treatment guidelines that prioritize safe drinking water at the household level while making use of agricultural byproducts and avoiding the need to import additional carbon from coal and coconuts for TCP extraction.

4.2 Materials and methods

We have divided the methods into subsections for P-POU tests and biochar isotherm batch tests. We use the same source water and procedure for spiking groundwater for both tests. We base our biochar particle size on the median size of filter material particles found in the point-of-use filters (SM Figure S1). Source water was collected from the tap at the University of California, Merced in California (Figure 16) as non-potable, untreated groundwater. Samples were kept in high-density polyethylene (HDPE) containers at room temperature throughout the experiment. Water samples were spiked with TCP to a concentration of or close to 200 ppt. This concentration was chosen for comparison purposes, as it was also used in a 2014 study conducted by the University of California Davis, which tested GAC from coconut shells and coal to reduce TCP levels (Mital, 2014).

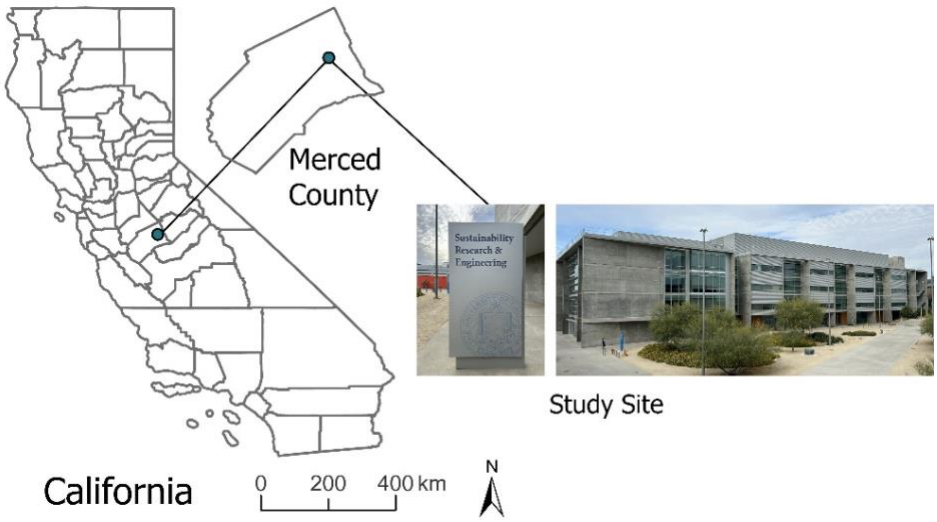


Figure 16 Site of tap water sampling. Sustainability Research Engineering Building, University of California, Merced, USA.

To create a spiking solution, volatile organics are sometimes carried in methanol. However, we chose an alternative method to dilute TCP that would better mimic how households use filters and avoid any possible chemical interference from methanol. A 120 mL glass amber bottle fitted with a mininert cap was filled with tap water then an air-tight Hamilton syringe was used to inject 1 ml of pure TCP into the bottle. Since TCP is a dense non-aqueous phase liquid (DNAPL), the injected TCP sank to the bottom of the bottle where it was visible. The bottle remained undisturbed in a fume hood for 48 hours to ensure a saturated TCP solution. The theoretical concentration of the solution was 1.75 g/L TCP, which is the solubility of TCP at 20℃ (USEPA, 2023). This saturated solution was then used to create the diluted solutions of approximately 0.2 μg/L needed for the P-POU and isotherm tests. For P-POU tests the diluted solutions were stored in a 50-liter HDPE plastic carboy. For the biochar isotherm, spiked solutions were made directly into the glass reaction flasks. Our methodology is published and can be found at the following link https://www.protocols.io/private/6CEA37765BC811EEA1C30A58A9FEAC02.

4.2.1 Pitcher point of use filters

Three types of pitcher point-of-use (P-POU) water filters were evaluated for their ability to remove TCP from tap water (Table 9). All filters use activated carbon with cation exchange resins, and pitcher 3 also contains an anion exchange resin (Anumol et al., 2015). The manufacturer's expected lifetime (MELs) for pitcher filters 1 and 2 is 151 L, while for pitcher 3, it is 85 L. Each filter was tested in triplicate.

Table 9 Manufacture's information on filter composition and usage timeframe.

Pitcher number	Filter composition	Filter lifetime (days)
1	Activated carbon granules; cation exchange resin	60
2	Activated carbon granules; cation exchange resin	60
3	Activated carbon granules; oxidation reduction alloy; anion-cation exchange resin	60

Before testing, each P-POU device was pre-conditioned according to the manufacturer's instructions (SM Table S2). Spiked water was added to P-POU filters in volumes of 1 liter and allowed to equilibrate for 30-60 seconds between additions. The experiments were carried out over ten working days with no water being added to pitchers over the weekend. We carried out the tests at room temperature (21.5 ^{o}C) and experiments were conducted in triplicate for each filter type. Filtered samples were collected when the percentage of water passed through the filters equaled 0, 25, 50, 75, 100, and 125% of the MEL for the filter. Additionally, the approximate flow rates for each of the three filters were measured during the experiment. One-liter samples were poured into the filter and timed until they passed through.

Control samples were taken when the filtered water was sampled. The control group consisted of pitchers without filters with the same contact time with spiked groundwater as the experimental groups. Because the filters vary in terms of lifetime and performance, we used two criteria to compare the efficacy of the different P-POU devices to attenuate TCP levels: 1) the individual removal efficiency (IRE) defined as the removal of TCP at a given sampling point along the MEL and 2) the lifetime individual removal efficiency (LIRE) defined as the average removal of TCP throughout the MEL (0–100% MEL). The removal efficiency percentage was calculated using the following

equation where C_{in} represents the initial influent concentration and C_{out} represents the effluent concentration of TCP.

$$\text{Removal Efficiency} = \left[\frac{C_{in} - C_{out}}{C_{in}}\right] \text{x } 100$$

To determine if the plastic on container walls absorbed TCP, we conducted tests using three Teflon-lidded glass containers and three polyurethane containers filled with tap water spiked with TCP. Since drinking water cups, bottles, and storage vessels are commonly made from HDPE plastics, understanding if and to what extent TCP sorbs to HDPE is important since TCP could also desorb and remobilize from HDPE surfaces. Additionally, the pitchers we used are all made of HDPE plastic, and the reported TCP removal percentages may be due, in part, to plastic sorption. The contact time was four days, after which each container was sampled and analyzed for TCP concentration. All effluent samples were capped with no headspace and sent to BSK labs in Fresno, California for analysis. An unpaired two-sample t-test (Helsel and Hirsch, 1992) was used to compare the mean of water spiked with TCP to understand if there is a significant difference in the amount of TCP sorbed to the plastic walls of a sealed container compared to the walls of glass containers.

To determine if there are any significant differences in the removal efficiency among various filter types, we conducted a Shapiro normality test and then used a one-way ANOVA analysis using R software. The ANOVA test is parametric, requires the data to follow a normal distribution, allows for smaller sample sizes and is suitable for comparing three or more groups. We also use unpaired t-tests to determine if there was a significant reduction in the concentration of the effluent from a specific filter compared to a control in which no filter was present.

4.2.2 Baseline water sample analysis

We tested the pH and conductivity of the sample water using a Mettler Toledo™ SevenExcellence™ S400 Benchtop pH Meter. Total dissolved solids concentration (TDS) was determined using the TDS meters provided with one of the tested pitcher systems. Sample water was analyzed for nitrate levels and total organic carbon (TOC) by BSK Labs in Fresno, California USA. Nitrate concentration and TOC concentration were determined using EPA method 300.0 and TOC method SM 5310C.

4.2.3 Almond biochar production and size sampling

The biochar was produced from almond shell feedstock by Dr. Hugh McLaughlin from NextChar for the University of California Merced. Biochar production occurred in a prototype continuous-feed rotary reactor called a mobile pyrolysis reactor. The temperature was kept at 350 ^{o}C with high residence time in a slow pyrolysis configuration. Biochar samples were sampled for particle size using a WS Tyler model RX-29 sieve shaker. We used biochar which passed through a US sieve size 18 (1 mm) but was retained on a US sieve size of 35 (500 µm). This size range was selected because it corresponded with the median size of particles obtained from a Brita filter (SM Figure S1). After selecting the appropriate size for the biochar, the sample was divided into

smaller portions using a riffle splitter to ensure that the isotherm tests were conducted on representative samples.

4.2.4 Biochar physical characteristics

The physical characteristics of biochar were examined at the Imaging and Microscopy Facility (IMF) at UC Merced. The Zeiss™ Gemini 500 Field Emission scanning electron microscope (FE-SEM) is a high-resolution FE-SEM that was used to analyze the size and distribution of macropores on the surface of the biochar from multiple high-resolution images. The mean distance between macropores was determined using image J software developed by the National Institutes of Health from twelve different images (Schneider et al., 2012). A Thermo Scientific™ Nexsa G2 X-Ray Photoelectron Spectrometer (XPS) was used to determine which if any elements and functional groups are present on the surface of the char. Five different biochar samples were scanned for surface chemistry features. XPS scans were made in both survey mode and high-resolution mode. The XPS 'survey' setting scans for all surface elements while higher-resolution scans provide data at a narrower range of binding energies. The binding energies of photoelectrons emitted from the surface of a sample are used to identify elements present. Binding energy signals were identified using the Thermo Scientific Material Science Data System for XPS (Thermofisher, 2021).

4.2.5 BET analysis

A Brunauer–Emmett–Teller (BET) analysis was carried out for the almond shell biochar using a surface analyzer (model Micromeritics Gemini VII 2390a) to produce N_2 BET-specific surface area results. First, the sample was dried at 110 ^oC for 2 hours prior to degassing. Degassing was performed with a Micromeritics FlowPrep 060 at 200 ℃ for 6 hours. N_2 gas was supplied as an adsorptive at 18 psi pressure using a two-stage regulator into a tube containing the sample and into a balance tube (static volumetric technique). Both tubes were submerged in cryogenic liquid N_2 and kept under identical conditions to achieve isothermal conditions. In a Gemini VII 2390a, a separate servo valve coupled to a differential pressure transducer regulates the flow rate of analysis gas into the balance tube. The adsorption of the analysis gas onto the sample causes the pressure difference between the sample and balance tubes and is detected by the differential pressure transducer. The servo valve repeatedly adjusts for the pressure drop by allowing additional gas into the sample tube. Gemini VII Version 5.03 software provided the isotherm and BET surface area using user-defined points.

4.2.6 Isotherm adsorption of TCP using almond-derived carbon

Isotherms are commonly used to determine the capacity of a sorbent for a particular sorbate (Brusseau and Chorover, 2019). Tap water with TCP was mixed with various amounts of prepared almond shell biochar and allowed to equilibrate to determine the maximum amount of TCP removed at a given temperature. The quantity of contaminant adsorbed per unit mass of sorbent versus the concentration of contaminant remaining in solution at equilibrium is used to compare carbon sources and optimize adsorbent use. Results from this analysis were compared to a previous study of TCP sorption efficiency with coal and coconut shell derived GACs (Mital, 2014). For the batch isotherm tests, we used a protocol based on the American Society for Testing and

Materials (ASTM) Standard Practice for Determination of Adsorptive Capacity of Activated Carbon by Aqueous Phase Isotherm Technique that we modified to minimize the loss of TCP via volatilization while handling, transferring, and storing solutions during the experiment (ASTM, 2020). These modifications include the use of filled glass bottles with no headspace and sealed with airtight Teflon caps; the agitation of glass bottles with glass beads for 48 hours; and substituting filtration with a 48-hour settling period following agitation. Additionally, the volatilization losses that do occur using control samples with no GAC are accounted for in removal calculations. The procedure was performed at room temperature (21.5 ℃).

The test flasks, caps, and glass beads were acid-washed (2M HCl) and then allowed to dry completely. Selected carbon amounts were added to each flask, capped, and massed. An approximate range of carbon mass estimated from published pure solute isotherm data required to bracket the adsorption of the TCP concentration used in this study was determined by selecting masses from the lower, middle, and top suggested masses from the ASTM. Three glass beads were added to each flask to increase agitation and the bottles were massed again. TCP spiked water from the HDPE container was then delivered into each flask to the brim so that there is no headspace and immediately covered with a Teflon cap. The volume of the water in the flask was determined gravimetrically. The flasks were then placed on a platform agitator at 250 rpm for 48 hours and then allowed to settle for 48 hours. Solutions were then loaded into 40mL amber vials containing a 1M hydrochloric acid preservative, capped with no headspace, and refrigerated at 4 ºC until transported on ice for analysis. Samples were analyzed at BSK Analytical Laboratory in Fresno, California using the Department of Public Health's Sanitation and Radiation Laboratories (SRL) method SRL524.2 liquid-chromatography and mass spectrometry (Okamoto, 2002).

4.2.7 Isotherm calculations

The chemical concentration of TCP which remains in solution after equilibration with biochar, and the mass of TCP adsorbed per unit mass of carbon (x/M) was determined. The mass of TCP adsorbed per unit mass of activated carbon was calculated by subtracting the final corrected effluent concentration using the equation:

$$\frac{x}{M} = \frac{[(C_O - C_f) + (C_O - C_B) * V]}{M}$$

x / M = mass of TCP adsorbed per unit mass of activated carbon, mg/g
C_O = initial TCP concentration, mg/L
C_f = TCP concentration in solution following adsorption, mg/L
C_B = TCP concentration in the solution of the control following adsorption, mg/L
$C_0 - C_B$ = TCP loss to volatilization, mg/L
V = sample bottle water volume minus carbon and glass bead volume, L
M = activated carbon mass added per sample, g
x = chemical mass adsorbed per sample, mg

The Freundlich isotherm was used to analyze the sorption data and determine the distribution of TCP between the adsorbed phase and solution phase at equilibrium. This

model is ideal for biochar and other adsorbents with a non-uniform surface, as it considers various adsorption energy sites and multiple layers of adsorption (Mital, 2014). The Freundlich isotherm equation is as follows:

$$q_e = K_f * C_e^{1/n}$$

q_e = mass of adsorbate per mass of adsorbent at equilibrium [µg/mg]
K_f = adsorption capacity [L/mg]
C_e = aqueous concentration of adsorbate at equilibrium [µg/L]
n = adsorption intensity parameter [unitless]

4.3. Results

4.3.1 P-POU results

During the MEL, we observed a slight decrease in the flow rates of Pitcher 1 and Pitcher 2 filters as indicated in Figure 17 and SM Table S3. We encountered inconsistent flow rates with Pitcher 3 due to frequent backups. To address this issue, we followed the manufacturer's recommendation by shaking the filter contents vigorously between influent additions after removing the filter from the pitcher base. This approach temporarily improved the flow rate before it slowed down again (up to 2 hours). Despite our efforts to enhance the flow rates through shaking, we were unable to use Pitcher 3 for the final removal percentage assessment at 125% MEL (Figure 18a) since it took over an hour to drain one-liter additions after the 100% MEL.

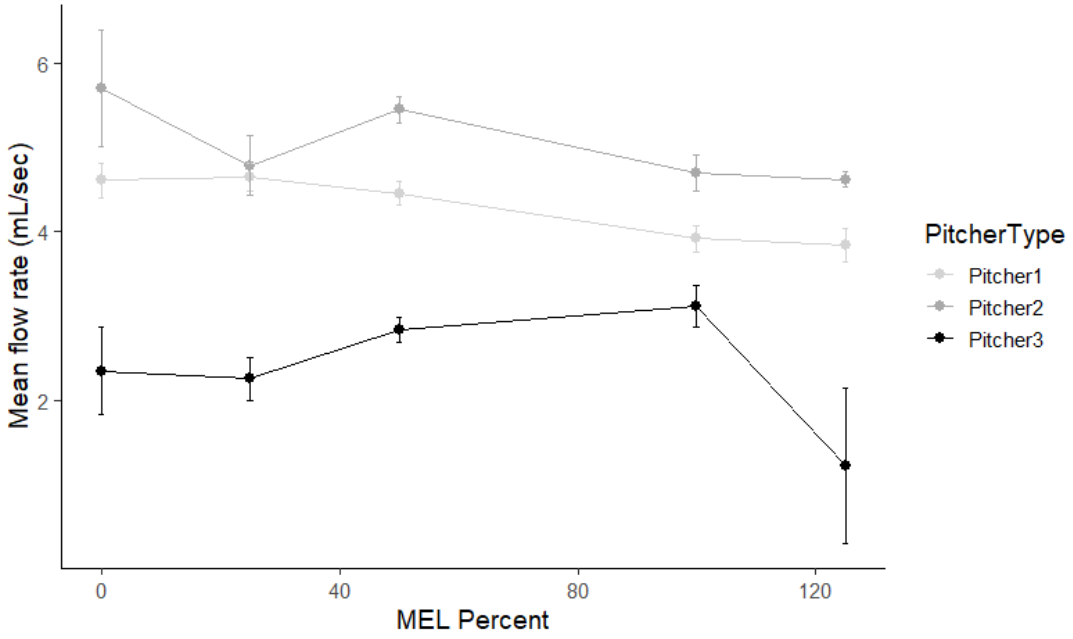
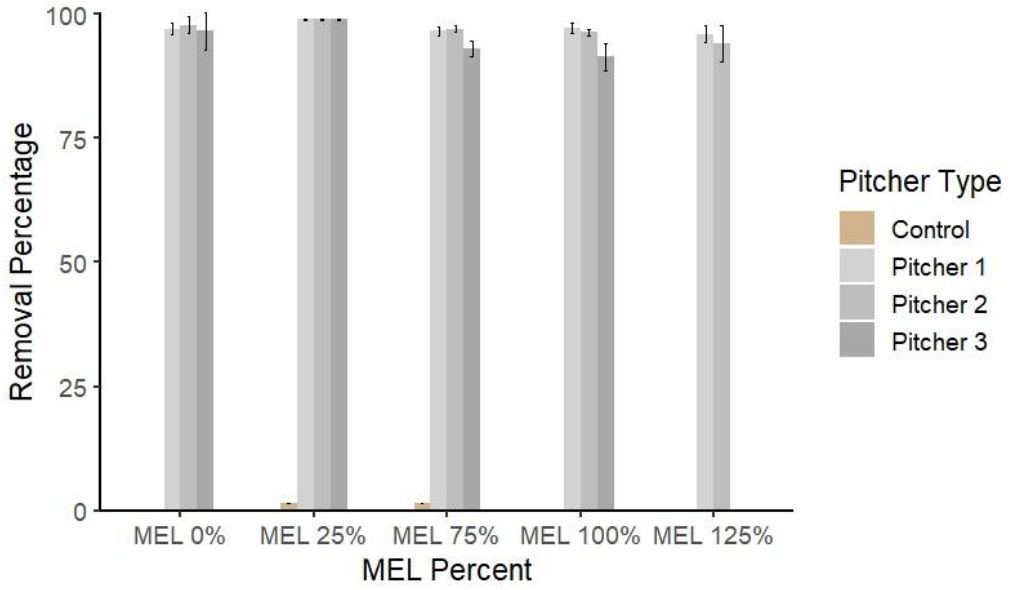


Figure 17 Flow rates for three pitcher point-of-use filters throughout the manufacturer's estimated lifetime (MEL). Error bars represent standard deviation (n=3).

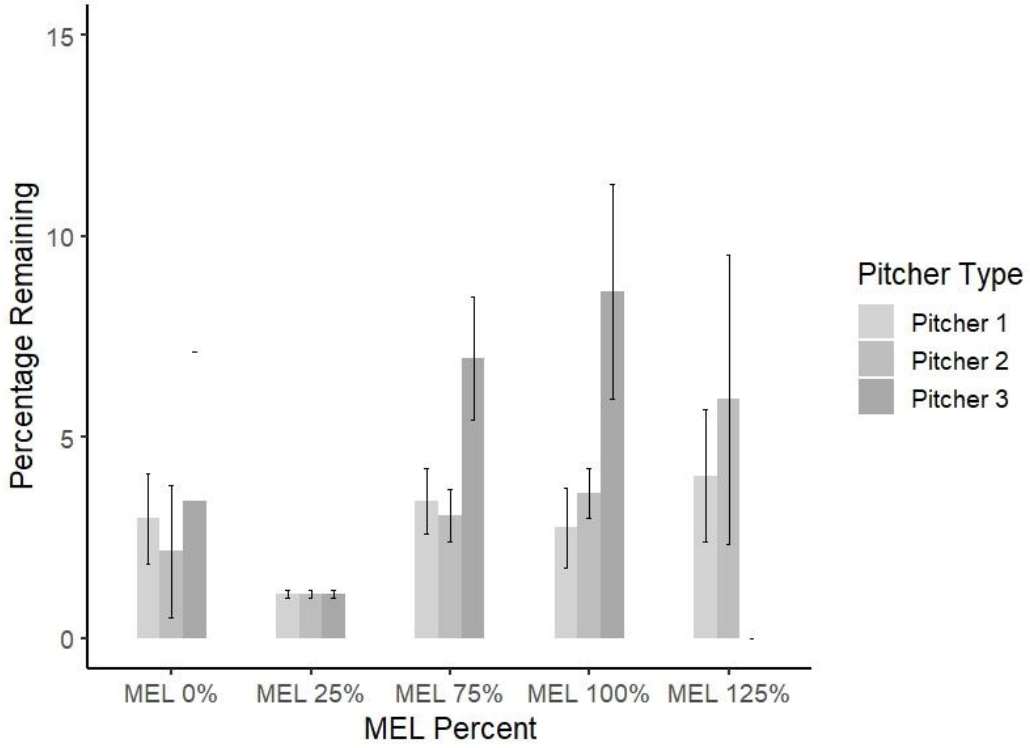
Although individual removal percentages showed a slight lifetime decrease for Pitchers 1 and 2, and a greater decline for Pitcher 3, all filters still maintained relatively high removal rates at the end of their lifespan (SM Table S4). At 125% of the MEL,

Pitcher 1 still removed over 95% of TCP and pitcher 2 removed over 90%. At 100% of the MEL (the last sampling point) pitcher 3 removed over 85% (see Figure 18a). The mean percentage of TCP removed during the lifetime of all three filters exceeds 98% (as shown in Figure 18b). After conducting an unpaired ANOVA test, we found no significant difference ($p = 0.8$) between the average removal percentages of the three filters.

a.



b.



c.

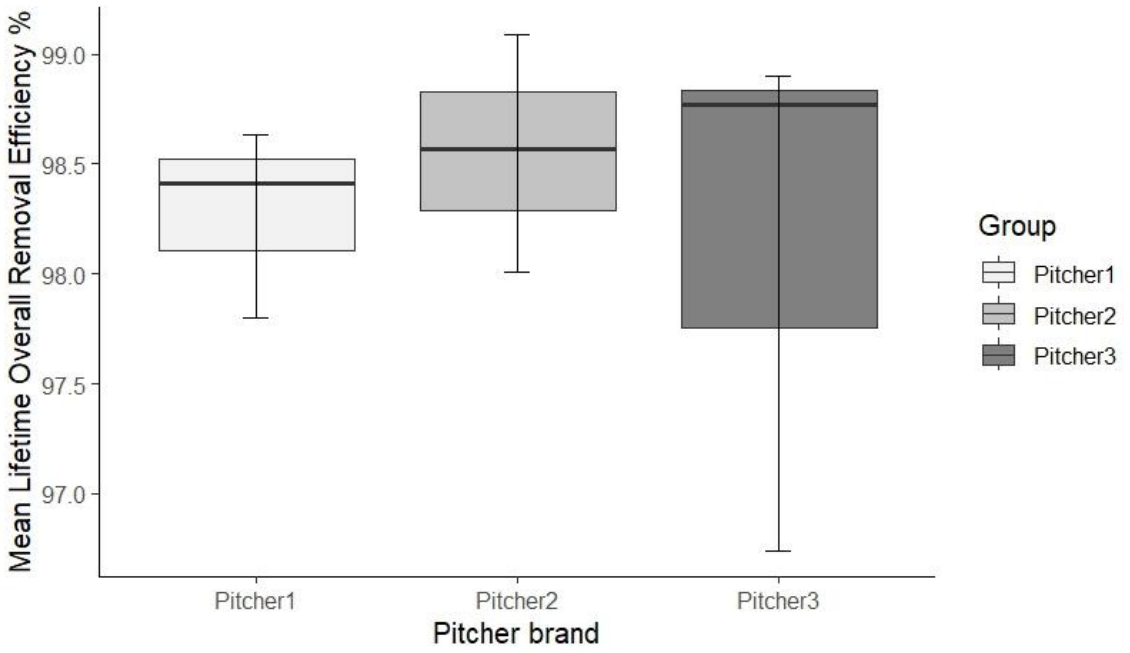


Figure 18 a. Removal efficiency of 1,2,3-trichloropropane (TCP) at sampling points along the manufacturer's estimated lifetime. b. Percentage of TCP remaining in effluent (100-a). Control (pitcher without filter) showed no significant volatilized loss compared to initial solution concentration. c. Mean lifetime (0-100%) removal of TCP for filter pitchers. a-c. Error bars represent standard deviation (n=3).

We conducted a cost analysis of diverse Point-of-Use (P-POU) devices, taking into account the cost of replacement filters and annual ownership expenses as outlined in Table 10. Our calculation methodology for annual pitcher ownership expenses involved considering the cost of a replacement filter. This estimation was made under the assumption that a family consisting of four individuals would utilize the filter for its entire Maximum Expected Lifetime (MEL). Additionally, we factored in a daily water consumption rate of 2 liters per person to ensure a realistic representation of usage patterns.

Table 10 Cost comparison of three different pitcher point-of-use filters used for this study

Pitcher number	**Filter lifetime volume [a] (L)**	**Filter cost [b] (US $)**	**Filter lifetime [c] (days)**	**Yearly filter replacement cost [c] (US $)**
1	151	7.99	19	155
2	151	10.99	19	213
3	85	14.99	11	515

[a] Manufacture's recommendation
[b] Estimated unit cost from online retailers on 09/01/2023
[c] Based on a family of four consuming 2 L/day each

4.3.2 Plastic sorption results

To determine if there was a significant amount of TCP sorbing to the plastic walls of a sealed container, an unpaired two-sample t-test was used to compare the mean of water spiked with TCP stored in plastic versus glass-sealed containers. The mean

concentration of TCP at equilibrium sampled from a plastic container was approximately 19% lower than a glass container, and an unpaired t-test revealed a statistically significant difference in the mean TCP concentration data (p=0.0008) between the two groups (Figure 19). A linear isotherm model applied to the equilibrium data indicates a Kd value of 1.3 L/g (SM Table S5).

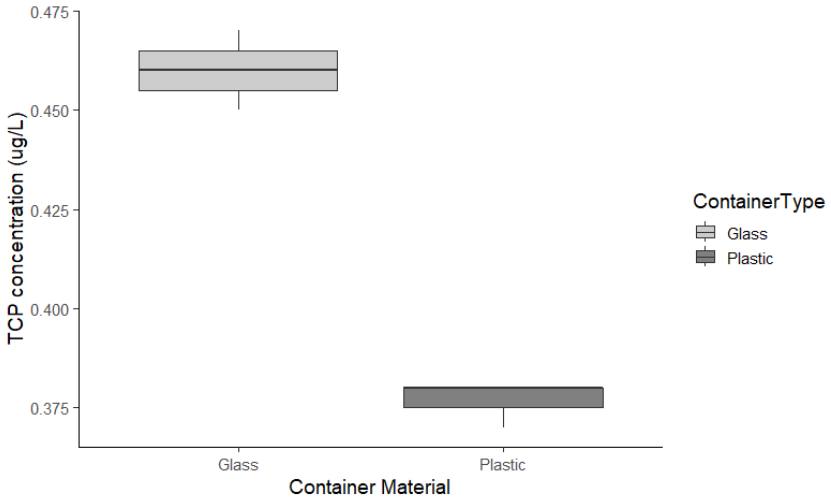


Figure 19 Mean equilibrium concentration of TCP stored in glass and plastic containers. Glass containers showed no volatile loss compared to a control group. Error bars represent standard deviation, n = 3.

4.3.3 Source water analysis

The pH of the source water used in this study was slightly basic, measuring 7.5, with a conductivity of 251 µs/cm at a temperature of 21.5 ℃. Nitrate levels were found to be near the federal maximum contaminant level, at 9.2 mg/L; the US Environmental Protection Agency (EPA) deems nitrate levels exceeding 10 mg/L (measured as NO_3-N) in drinking water as harmful (USEPA, 2021). Total organic carbon (TOC) levels were detected at 0.215 mg/L, and the total dissolved solids measurement was recorded at 104 mg/L (SM Table 1).

4.3.4 Almond biochar surface features and functional groups

Using multiple SEM images at 400-1,000x magnification for seven different char fragments we measured the mean length of macropores on the char surface. The mean macropore length, 19 microns, was measured with Image J software with 25 macropores measured per sample (SM Figure S5). As the macropores are not circular, the largest diameter across any given pore was selected for the measurement. Differences between the groups, as indicated with a one-way ANOVA statistic, indicate significant ($p<0.05$) differences in the mean length of macropores from sample to sample ($p<0.5$).

Using XPS plots for Binding Energy (eV) on the x-axis and measured photoelectron counts on the y-axis, we identified the following groups and elements given the binding energies: C=O (a carbonyl group), C-O (alcohol or an ester), C-NH_2 (amine), Calcium (Ca), and Potassium (K). XPS data are in the form of spectral plot data in either survey mode or high-resolution mode.

4.3.5 BET analysis results

Table 11 shows the N_2 BET-specific surface area and pore volume for the almond biochar used in the batch isotherm tests. The surface area value of 1.21 m^2/g is low but the micropore area (less than 2 nm pore size) comprises 58.3% of the total area. The single-point adsorption total pore volume is also low at 0.00028 cm^3/g. In a study of GAC adsorption using multiple commercial coal and coconut based granular activated carbons the surface area ranged from 780 – 1390 m^2/g for coal and from 970 – 1050 m^2/g for coconut; total pore volume ranged from 0.391 – 0.728 cm^3/g for coal and 0.461 – 0.464 m^3/g for coconut shell carbon GACs (Crincoli et al., 2020).

Table 11 BET Specific Surface Area and Pore size parameters for almond biochar

Material	**Specific Surface Area (m^2/g)**	**t-plot Micropore Area (m^2/g)**	**Single Point Adsorption Total Pore Volume (cm^3/g)**	**t-plot Micropore Volume (cm^3/g)**
Almond shell biochar	1.21	0.70	0.00136	0.00028

4.3.6 Almond biochar TCP isotherm

The isotherm data were plotted on a log-log scale (Figure 20a). The TCP concentrations (µg/L) remaining in solution after equilibration with activated carbon (Ce) were plotted on the horizontal (x) axis; the masses of TCP adsorbed per unit mass of activated carbon (µg/g) were plotted on the vertical (y) axis. The resulting K_f value is 0.032 (Table 12).

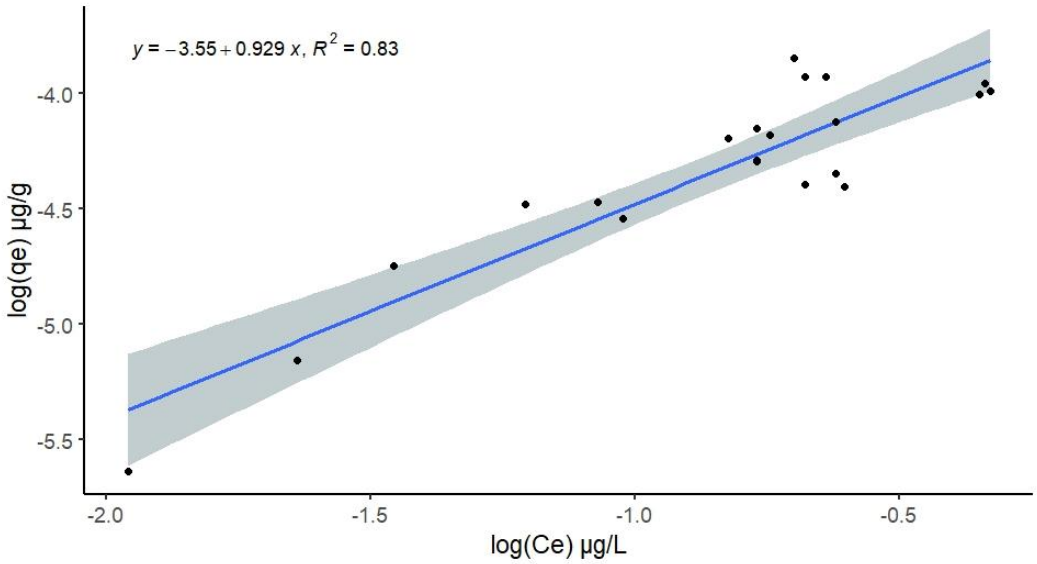
Table 12 Freundlich isotherm parameters from this study for almond biochar compared to those for coconut shell and coal-based carbon sorbents (Mital, 2014)

Sorbent material	**Log K_f**	**K_f, µg/mg • $(L/\mu g)^{1/n}$ (95% Confidence interval)**	**1/n (95% Confidence interval)**
Almond biochar	-3.55	0.029 (0.025-0.040)	0.99 (0.51 – 1.29)
*Coal GAC	-1.05	0.090 (0.057-0.14)	0.367 (0.25 – 0.49)
*Coconut GAC	-0.62	0.24 (0.071 – 0.82)	0.574 (0.29 – 0.86)

* Values from Mital, 2014.

A comparison of the isotherm at low concentrations was conducted for the three sorbents shown in Table 12 as experimental data collected for the almond shell biochar was not achieved due to difficulty in making TCP solution concentration in the desired range. For solutions at 0.2 µg/L, Freundlich parameters were employed to estimate the distribution coefficient, Kd, representing the extent of TCP sorbed to the carbon relative to the TCP concentration in the solution. This measurement helps determine the affinity of a chemical for solid versus aqueous materials. The resulting Kd values for almond biochar, coal, and coconut were 0.029, 0.092, and 0.27 respectively. Notably, almond biochar exhibited an estimated Kd value one order of magnitude lower than that of coconut shell GACS.

a.



b.

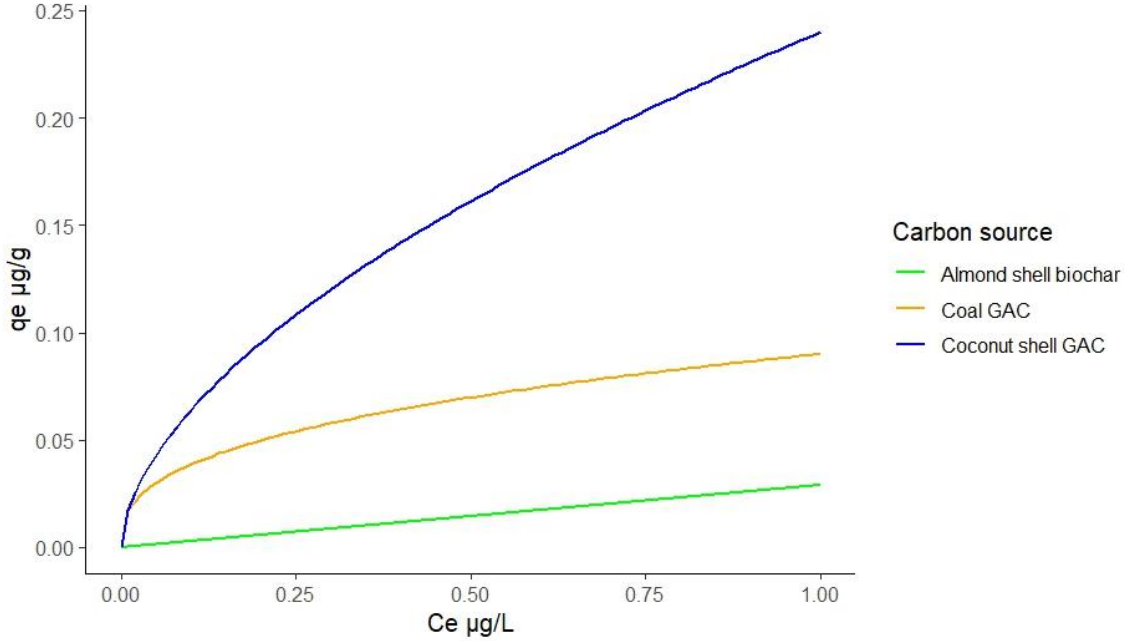


Figure 20 a. Linearized Freundlich adsorption isotherm (blue) and experimental data for the adsorption of 1,2,3-trichloropropane (TCP) on almond biochar. The error band represents a 95% confidence interval. Performed at 21.5 ℃. b. Comparison of three different carbon isotherm models using parameters from table 12.

4.4 Discussion

We evaluated the lifetime removal efficiency of three P-POU filters that use GAC and found them to be highly effective; the mean lifetime (0-100% MEL) removal efficiency of all three P-POU filters tested remained above 98% (Figure 18b). This information is especially important for households that rely on domestic wells and that do

not have filtration systems. While P-POU filters are a cost-effective option, it's worth considering that larger families may find the slow flow rates (as shown in Figure 17 and SM Table S3) and the cost of filter replacements challenging. However, filters are less costly than bottled water from both an income and environmental standpoint (Cohen, 2018) and could be subsidized by the state, city, or county for districts above the MCL. At an average cost of $1.23/gallon, the yearly cost of buying bottled water for a family of four drinking 2 L/day ($714) is over four times more than the yearly filter replacement cost for the least expensive filter that we tested ($155). Moving forward, we recommend additional testing of under-the-sink and refrigerator filters to determine their effectiveness in removing TCP and including their yearly replacement costs for comparison. We also recommend further analysis of almond GAC at a larger municipal or household private-well scale as a more cost-effective and sustainable option in the Central Valley and beyond.

While carbon-based P-POU filters have demonstrated efficacy in reducing the concentration of various organic contaminants (Bansode et al., 2019), it's important to acknowledge their inherent limitations. These filters are not specifically engineered to remove bacteria or lower nitrate concentrations. Consequently, bacterial proliferation within the filter can occur, leading to heightened bacterial levels in the filtered water (Wu et al., 2017). GAC filters, in particular, are susceptible to biofilm formation, primarily due to the adsorption of microbes from water. Over time, these microbes adhere to the GAC surface, gradually forming biofilms (Shi et al., 2023). Within the porous structure of activated carbon, microorganisms find ideal conditions for growth, fueled by the organic matter they absorb. Moreover, periods of water stagnation during regular use can exacerbate biofilm growth (Shi et al., 2023), especially concerning when filtering water from private wells, which may harbor higher concentrations of microbial contaminants, including pathogens (Mulhern et al., 2021). Biofilms pose a significant risk to water quality in POU Systems, as they can release bacteria if filters with attached biofilms are not replaced regularly, resulting in elevated bacterial concentrations in the filtered water. Additionally, the adsorption capacity of carbon point-of-use filters for nitrate and nitrite is relatively low (Mazarji et al., 2017). Given that wells contaminated with TCP often also contain nitrates due to agricultural activities, P-POU filters may require supplementation with reverse osmosis or ion exchange units to effectively reduce nitrate and nitrite levels (Mazarji et al., 2017).

Regarding the almond biochar batch tests, our results give a TCP-biochar K_f value of 0.032, which is less than that of coal (0.090) and coconut shell (0.24) GACs used in previous batch isotherm studies and currently in use by water utilities to remove TCP (Table 3) (Mital, 2014). However, lower efficiency is not unexpected as the biochar has not been activated by steam and/or carbon dioxide as commercially prepared GACs are treated, and we did not run multiple tests with differently prepared biochar to optimize char selection. A non-zero K_f value shows that there is potential for TCP sorption; fine-tuning of nutshell biochar and chemical or physical activation may improve biochar efficiency to potentially replace or supplement commercial carbon GACs.

SEM analysis of the almond biochar showed significant ($p<0.05$) differences in the mean length of macropores from sample to sample and indicated a heterogenous topography of the char. While our study provides valuable insights, there are opportunities for further research. For instance, we recommend exploring the use of char

made under different conditions, such as higher temperatures and longer pyrolysis times, to identify the char with the highest sorption profile. Additional tests may also include coating the char with elements such as zinc, which has been shown in other studies to effectively degrade TCP via chemical reduction (Sarathy et al., 2010). This study was an initial proof-of-concept to see if further exploration would be beneficial.

Moreover, we used XPS analysis to identify electronegative carbonyl group (C=O), alcohol or an ester (C-O), amine (C-NH_2), and the metals Calcium (Ca), and Potassium (K) on the char surface. The intermolecular attraction of the TCP and char surface may be facilitated between electronegative chlorine atoms in TCP and electropositive Ca and K. We suggest exploring other metals such as zinc as a char coating since zinc has been shown to reductively eliminate TCP in solution in numerous studies (Hauptman and Naughton, 2021).

Biochar properties depend on a variety of factors. The sample we tested had low values of specific surface area and pore volume compared to other types of biochar available. This is because the properties vary in samples based on pyrolysis temperature and the characteristics of the biomass feedstock. The almond shell sample used in this experiment was produced by a prototype pyrolyzer called '1x mobile pyrolysis unit'. It is a prototype rotating unit that operates at around 350 ℃. The lower operating temperature could be the reason for the low specific surface area and micropore volume. At this temperature, volatiles are expected to remain in the structure of the biochar in large amounts. Generally, as the process temperature increases, the amount of volatiles removed increases.

4.5 Conclusions

This study tested almond biochar and pitcher filters for the removal of TCP from groundwater spiked with TCP. The outcomes of this research provide valuable insights to almond producers, utilities, and communities regarding household treatments while attempting to minimize the reliance on imported carbon for TCP removal. The research objectives support UN Sustainability Goals 3 and 6 targeting safe and affordable drinking water for all and a reduction in illnesses from pollution.

Of the three pitcher filters tested, there was no significant difference between the different filters' ability to remove TCP from sample groundwater. All filters maintained relatively high removal rates for the lifetime of their use. Given these results, future research is needed to determine if removal rates remain high with different drinking water sources such as those that have higher TOC levels, co-contaminant concentrations, and different water chemistry. This understanding will help target locations where filter pitchers may be considered for use by water consumers. Additionally, the results of this work should be considered by pitcher filter certifiers. Given the widespread contamination of drinking water sources by TCP, NSF/ANSI certification could be expanded to include TCP.

Batch tests show that almond biochar has lower TCP sorption effectiveness compared to granular activated carbon derived from coconut shells or coal. Subsequent research could explore variations in char production conditions, like extended heat durations and increased heating temperatures, to evaluate their impact on sorption efficiency. Investigating these factors may provide insights into optimizing char performance for contaminant removal applications.

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Chapter 5. Unsafe at Low Levels: Adopt a Federal MCL for 1,2,3-Trichloropropane in United States' Drinking Water[(c)]

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Executive Summary

1,2,3-richloropropane (TCP) is a toxic, man-made chemical used widely in agricultural and other contexts from the 1940s to the 1980s. TCP has settled into groundwater supplies nearly everywhere it was used. In 2009, the Environmental Protection Agency (EPA) included TCP on the Third Contaminant Candidate list (CCL3) and listed the safe oral reference dose (RfD) for TCP at 0.004 milligrams per kilogram per day. Since then, we have learned that the scope of the TCP contamination problem is greater than first understood. At least 13 states and one territory have contaminated wells. Animal studies show that TCP is a potent carcinogen, and toxicology studies suggest that TCP is unsafe at levels at and above its 5 ppt detection limit. Three states, California, Hawaii, and New Jersey have adopted enforceable maximum contaminant levels of TCP in groundwater. As other states become aware of contamination levels, it is likely that some of them will also regulate TCP, but that could take many years. Federal legislation could mandate EPA advisories sooner than state legislation. The EPA has used the detection limit as the maximum for at least one other chemical, 1,2-Dibromo- 3-chloropropane (DBCP), a common co-contaminant of TCP. We recommend that the EPA adopt TCP's lowest detection level, 5 ppt, as the federal maximum contaminant level

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5.1 The problem: contaminated tap water

For many Americans, the water they drink, cook with, and bathe in is polluted with unsafe chemicals. While the federal government has created national regulations for some chemicals such as lead and polychlorinated biphenyls (PCBs), much regulation is done state-by-state, resulting in inconsistent policies that are often administered inequitably. Those inequities become clear when we look at the communities most impacted by toxic water, including rural and marginalized communities facing other inequities, such as limited access to healthcare and other basic services (Balazs and Ray 2014; Schaider et al. 2019).

Inconsistency in the regulation of harmful chemical pollutants results in limits that are either set too high or lacking altogether. The history of 1,2,3-trichloropropane (TCP) makes clear the potential consequences of this type of regulation, or lack thereof. Some states including California, Hawaii, and New Jersey have set MCLs for TCP at 5, 600, and 30 ng/L, respectively (U.S. EPA 2017a; Torralba-Sanchez et al. 2020). The

MCL of these three states differ by up to two orders of magnitude and illustrate the need for a national regulation so that all consumers are protected at the same risk level.

Used as an industrial solvent, injected into the soil, and included as a component in widely used pesticides, TCP had been spreading for years before the scientific community recognized its deleterious effects. As a result, people, often in marginalized communities and rural agricultural outposts, had been drinking water contaminated with TCP long before Hawaii, California, and New Jersey set state maximum contaminant levels (MCL) and required that water systems are regularly monitored to detect its presence.

Once thought of as an emerging contaminant, TCP is now understood to be carcinogenic and because it is ubiquitous in groundwater near agricultural regions, this issue demands federal oversight (Kielhorn et al. 2003; Burow et al. 2019). A World Bank report "Quality Unknown," identified fragmented regulations across countries and agencies as a cause for uncertainty, and a hindrance to progress toward universal clean and accessible drinking water (Damania et al. 2019). TCP meets all the statutory criteria that the EPA uses when it considers whether to regulate a chemical, as required by The Safe Drinking Water Act (SSDWA 1996; EPA 2021.):

- TCP is a recognized carcinogen with adverse health effects (Kielhorn et al. 2003).
- TCP occurs in public water systems in at least thirteen states and one U.S. territory.
- Federally regulating TCP would be a "meaningful opportunity" to reduce health risk.
- for consumers especially in marginalized rural agricultural communities.

5.1.1 Uses and prevalence TCP

TCP is a chlorinated organic pollutant that contaminates drinking water in areas where it was applied. Since it does not readily bind to soil and is highly stable, TCP has leached into groundwater and persists (US EPA 2017a). In 1970, the California Department of Food and Agriculture began listing fumigants with TCP in pesticide use reports, ultimately connecting TCP to more than forty crop types (CDFA 1970-1984).

Because TCP is on the third Candidate Contaminant List 3 (CCL3), it is part of the EPA's third Unregulated Contaminant Monitoring Rule (UCMR) which assesses the breadth of population exposure levels. For twelve months between 2013-2015, the EPA program sampled all public water systems serving more than 10,000 people and 800 representative systems serving 10,000 or fewer people (U.S. EPA 2012; U.S. EPA 2017b). The data showed that TCP was present in groundwater at levels above the California's Public Health Goal (0.7 ppt) in Alabama, Arizona, California, Connecticut, Florida, Hawaii, Maryland, North Carolina, New Jersey, New Mexico, New York, Pennsylvania, Puerto Rico, and Virginia (U.S. EPA 2017c) (Figure 21).

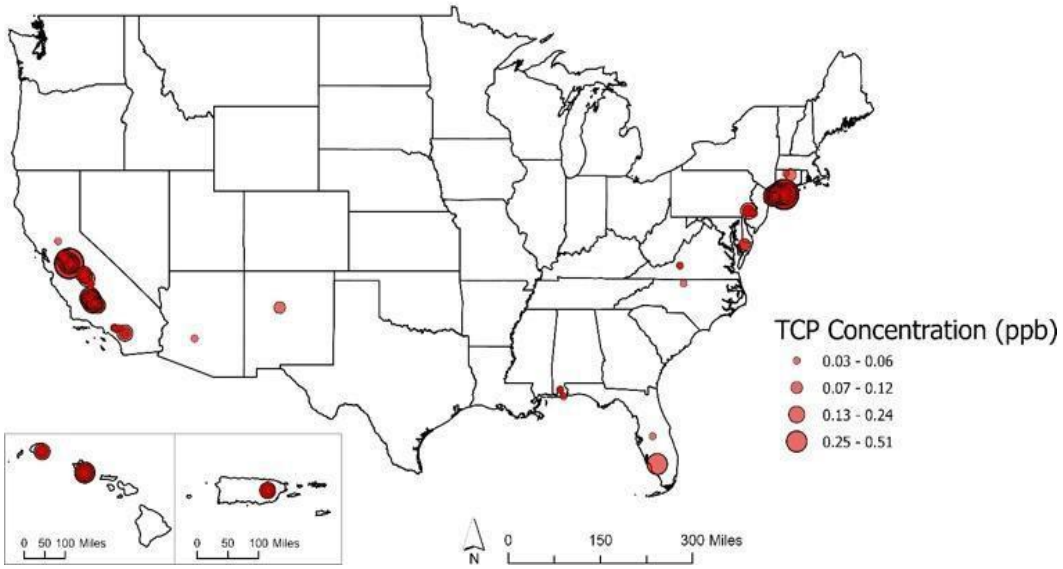

Figure 21 Map showing U.S. locations which have detected 1,2,3-trichloropropane (TCP) levels in groundwater. Hawaii (left) and Puerto Rico (right) are in the inset. TCP concentration in parts per billion (ppb) or µg/L. Data from EPA, (UCMR, 2013-2015).

5.1.2 Harmful effects of TCP exposure

As early as 1985 evidence began to show TCP's potent mutagenic properties in mice and rats when delivered orally or via inhalation (Villeneuve et al. 1985). In 1993, the U.S. National Toxicology Program (NTP) two-year chronic toxicity study showed "clear evidence of carcinogenic activity" in both male and female rats (NTP 1993). Although toxicity studies focus on TCP's carcinogenic potential, studies from both the World Health Organization and the EPA indicated that ingesting TCP can significantly reduce fertility and reproduction in mice (Keilhorn et al. 2003; U.S. EPA 2009).

On the heels of the NTP study, Irwin et al. (1995) published the first peer reviewed academic study of TCP's carcinogenic potential. They chose their dose range to mimic human occupational exposure based on the Occupational Safety and Health Administration (OSHA) limit: 10 ppm for an 8-hr. workday. The study showed that TCP induced a carcinogenic response even at the lowest doses (3 mg/kg for rats and 6 mg/kg for mice). Irwin et al. (1995) theorized that, given the high levels of mutagenic activity in the low dose groups, even smaller amounts of TCP would have induced cellular changes.

La et al. (1996) discovered that when TCP was delivered orally to mice and rats, tumors developed in multiple sites including the liver, stomach, and kidneys. The incidence of TCP-induced forestomach tumors was nearly 100%, even among the low-dose group (3 mg/kg for five days in mice and 6 mg/kg for five days in rats), when delivered orally via oil suspension. Although more information is needed regarding prolonged exposure in humans, La et al. (1996)'s findings confirm that TCP is carcinogenic even at the typical low doses found in tap water.

In the most recent study of TCP toxicology, Tardff et al. (2010) used a biological risk assessment approach to estimate Drinking Water Equivalent Levels (DWELs) for a lifetime of consumption. Tardff et al. (2010) used an internationally recognized

framework from the World Health Organization and the EPA to estimate, from animal models, safe TCP exposure levels for humans over a lifetime. They concluded that to protect against non-cancer toxicity and cancer, tap water can be consumed safely at TCP concentrations up to 200 ppb or micrograms per liter; however, the EPA's Integrated Risk Information System (IRIS) lists chronic oral reference dose (RfD) of 4 x 10-3 milligrams per kilogram per day (mg/kg/day). A RfD estimates the amount of a substance a person can be exposed to without adverse health effects over a lifetime of daily exposure (U.S. EPA n.d.). For comparison, a 62 kg person (average human weight) drinking 3 liters of water a day of water contaminated with 200 ppb would be equivalent to a comparable level of approximately 0.01 mg/kg/day or almost 2.5 times the EPA's RfD (Walpole et al. 2012).

5.1.3 Clean-up and co-contamination

Removing TCP from drinking water is costly. Del Rey, California – a small unincorporated rural community would have to install four filtration units to remove all of the TCP from their groundwater supplies at a total estimated cost of more than $18 million dollars (Klein, 2018). The Best Available Technology (BAT) is to pump and then treat contaminated water by passing it through Granular Activated Carbon (GAC). However, the carbon source must be replaced relatively often since GAC has a low affinity for TCP (Hauptman and Naughton 2021). TCP is a common co-contaminant with 1,2-Dibromo-3-chloropropane (DBCP), which is also treated with GAC (Burow et al. 2019). Like TCP, DBCP is another legacy contaminant no longer used but persistent in the environment due to its long half-life and low natural attenuation. Also a soil fumigant, DBCP is carcinogenic and can cause serious declines in male fertility including sterility (Teitelbaum 1999). The federal MCL for DBCP was set in 1991 at 0.2 ppb (U.S. EPA 2002).

5.2 Stakeholders

The EPA administrator, EPA scientists and decision makers, and members of the U.S. Senate Committee on Environment and Public Works should work together to advance TCP from the CCL stage to a federal MCL. Those living in or near agricultural areas are the most at risk of drinking water contaminated with TCP from non-point source contamination (Burow et al. 2019). There are also some communities near point source contamination from industrial use. For example, groundwater in southern California's San Fernando Valley superfund site called the Burbank Operable Unit has levels of TCP above the California MCL due to decades of aerospace manufacturing (Book and Spath 2007).

California's impacted cities are funding clean-up with money from legal settlements rather than passing costs off to consumers. In 2011 Livingston, California settled a lawsuit for 9 million dollars against two chemical companies to fund TCP clean-up efforts (North 2011). After a four-month trial in 2019, the City of Atwater, California was awarded $63 million to treat TCP contaminated groundwater after suing Shell Oil Co (Schlesinger 2019). A federal MCL would remove uncertainty about TCP safety and any doubts that it must be removed from the drinking water supply. Chemical companies that marketed fumigants containing TCP to farmers may wish to avoid costly litigation and might oppose a federal MCL for this very reason.

5.3 Regulatory background

The Safe Drinking Water Act (SDWA) regulates drinking water in the United States and gives the EPA the power to enforce National Primary Drinking Water Regulations (NPDWR) for specific contaminants and to determine the legally enforceable limit (MCL). There are seventy-eight substances with a federal MCL, but nothing has been added to the list since the SDWA was amended in 1996 (Fedinick et al. 2017).

5.3.1 EPA Rulemaking

Section 1412 of the SDWA outlines three phases to establish a Federal MCL for a new contaminant: 1) Identification, 2) Evaluation and 3) Regulation. For TCP, the EPA collected national occurrence data from 2013-2015 but since then the agency has not taken any further formal regulatory steps forward. The EPA also has yet to publish a national map showing where groundwater tests positive for TCP. During the second phase, evaluation, the EPA uses three criteria to decide whether they should start to develop a new NPDWR: health risk, high occurrence, and the reduction of risk. If the EPA Administrator determines that those criteria are met, it proceeds with regulation (U.S. SDWA, Section 1412, 1996). Multiple studies show TCP's potential to cause cancer and UCMR monitoring has been available for six years showing contamination in over a quarter of U.S. states and Puerto Rico (U.S. EPA 2017c). GAC, California and Hawaii's BAT for TCP, is a well-known and tested technology which can lower TCP levels to the detection limit (Babcock et al. 2018). It is past time for the EPA to move TCP to the third phase: regulation.

5.3.2 State regulations

In lieu of a federal MCL some states have established their own MCLs to protect consumers from TCP. Hawaii, New Jersey, and California have set MCLs at 600 ppt, 30 ppt and 5 ppt respectively (Torralba- Sanchez et al. 2020). California requires public wells above the limit to provide an approved treatment such as GAC; discontinue use of the well; purchase water from another utility; consolidate with other water systems; or dilute water to below the MCL (SWRCB 2018). California's strict regulations should be a blueprint for the EPA to follow.

5.4 Policy options

There are three policy options for the EPA's consideration. Option A presents the least risk for U.S. citizens and the highest potential treatment costs whereas option C has the greatest health risk. A federal TCP regulation may mean that some water systems may not have to install a new treatment system as one may already be in place for DBCP, a common co-contaminate with TCP.

i. Option A: The EPA should adopt the lowest detection limit (5 ppt) as the MCL for TCP. This provides the highest level of protection for citizens who depend on groundwater for drinking water.
ii. Option B: Adopt a higher MCL for TCP like New Jersey and Hawaii (30-600 ppt), which would mean lower implementation costs and an increase in the safety of drinking water sourced from groundwater in heavily impacted wells.

iii. Option C: Increase national testing especially in rural agricultural areas to better understand the distribution of TCP in groundwater supplies. Using this data, heavily impacted states should be advised to establish state level MCLs.

5.5 Recommendation

The EPA should adopt policy Option A to establish a federal MCL of 5 ppt for TCP. For chemicals thought to cause cancer the EPA sets the Maximum Contaminant Goal (MCLG) at zero; in other words, no amount of the substance in drinking water is considered acceptable. The MCL for TCP should be based on the lowest concentration that can currently be measured, which is 5 ppt. A federal MCL at the lowest possible detection limit, like that established in California, provides the most meaningful reduction in health risk for consumers (U.S. SDWA, Section 1412, 1996).

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Chapter 6. Conclusions

The goal of this dissertation is to understand how to best remove TCP from water supplies and where to best concentrate those efforts. The research fills unexplored gaps in the existing literature by conducting a systematic review of treatment technologies, performing a mass balance calculation for TCP in California groundwater, introducing machine learning models for a volatile contaminant, and exploring cost-effective sorption methods. The outcomes of this research contribute to knowledge and best practices to remove TCP from drinking water supplies, provide a more complete picture of the agricultural contributions to TCP contamination, and inform underserved communities on how well inexpensive and commonly used household pitcher point-of-use filters remove TCP from drinking water.

The systematic review (Chapter 2) finds that GAC, bioremediation, and ZVZ are currently the most effective technologies to reduce TCP levels and meet regulatory requirements for drinking water. However strong oxidants like persulfate have also removed high levels of TCP and an ammonia treatment shows high rates of TCP reduction in soil. Chapter 2 also used available literature to map global contamination sites in North America, Europe, and Asia and identified lack of studies in Africa and X. The mass balance and predictive model (Chapter 3) indicates that TCP accumulation in California groundwater from past fumigant use may be as high as 110,000–4,300,000 kg over a 30-year application period. It also shows that in California's Central Valley, the Random Forest machine learning algorithm is the top performer in predicting TCP contamination among tested machine learning models. Modeling also indicates that precipitation, redox state, and nitrate concentration are the most important explanatory predictors with the highest modeled TCP levels predominantly in disadvantaged communities.

The evaluation of almond biochar as a feasible carbon stock material for carbon sorption treatments (Chapter 4) shows the potential to remove carbon but less than GACs made from commercial carbon sources such as coconut and coal. However, biochar sorption is highly dependent on the conditions that produce the char, and therefore more research is needed. Additionally, a Life Cycle Assessment comparing biochar to coconut and coal-based carbon sources may reveal that although less efficient from a sorption perspective, local biochar may be more energy efficient than importing other carbon feedstocks. Chapter 4 also finds that using simple pitcher point-of-use treatments with carbon filters for removing TCP from tap water can be an effective method for reducing the amount of TCP in drinking water supplies. Testing three common brands finds no significant difference in the efficiency between brands. More testing needs to be conducted to show how total organic carbon levels affect the efficiency of point-of-use filters.

Finally, through an analysis of existing policy and toxicology research data, I make suggestions in Chapter 5 for future policy decisions. Evidence from animal models shows a clear connection between ingesting TCP and the development of various types of malignant tumors in numerous organs. I show a need for the establishment of a federal maximum contaminant level at the lowest analytical limit given how little is understood about chronic exposure to TCP in drinking water and the lack of monitoring data in much of the United States.

6.1 Future research

There is still much to understand about the distribution, removal, and health impacts of TCP contamination in the water supply. While current studies show that TCP is likely a human carcinogen, conducting epidemiological studies, such as cancer cluster studies, in areas like the San Joaquin Valley could deepen our knowledge of the health effects of consuming TCP-contaminated water. Similar research on Nitrate contamination in drinking water has shown a link between consuming nitrate levels above the MCL and thyroid cancer (Tariqi & Naughton, 2021; Ward et al., 2010)

Although this research maps available TCP data globally, there is little information about TCP contamination in much of the world. Future research could increase TCP monitoring (especially in areas of the world with agricultural land use in the latter half of the 20th century) and in areas that rely on groundwater for drinking water. A complete global map of TCP contamination requires more sampling, testing, and monitoring. Agricultural regions, chemical manufacturing sites, and military establishments are all areas of concern. To narrow down areas with higher contamination odds, machine learning models used in this research could be extended to other parts of the world. Knowledge regarding industrial point source contamination should also be included in these models for a more complete picture of impacted groundwater if data is available. Beyond decision trees, other machine learning models such as artificial neural networks (ANN) could also be tested for their ability to predict TCP in groundwater. Several studies have used ANN to predict nitrate leaching in groundwater (Al-Mahallawi et al., 2012; Ostad-Ali-Askari et al., 2017; Stylianoudaki et al., 2022).

Regarding alternative filter material and point-of-use filters, more information is needed to understand how the efficiency of point-of-use treatments changes with different water sources and other co-contaminants. The impact of total organic carbon levels on filter performance should also be investigated. Furthermore, under-the-sink filters and refrigerator filters could also be tested and compared to the results of this research. Other biochar made from different agricultural waste feedstocks may prove more effective than almond shell biochar. Different biochar preparation methods such as temperature and heating time to improve adsorption should also be explored. Future research should explore combined treatments using biochar or GAC treated with zero-valent zinc, which has the potential to effectively immobilize and reduce TCP.

Finally, there is a lack of community-based participatory research regarding TCP contamination. Conducting community surveys, interviews, and analyses would shed light on what impacted consumers want to know about TCP contamination and could be used to guide future research questions. These community connections would also provide a way to communicate scientific data back to water consumers.

6.2 Chapter 6 References

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Appendix 1: Supplementary Information for Chapter 2

Supplementary Material: Legacy 1,2,3-trichloropropane contamination: a systematic review of treatments

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Table S1 Results from a search of four online databases for 1,2,3-Tricholoropropane.

Database	Number of Results searched on 9/6/20
Science Direct	795
Web of Science	166
Pub Med	103
Engineering Village	96
Total from 4 databases searched	1,160
Duplicate Citations*	199
Total with Duplicates removed	965
Records screened by title and abstract	965
Records excluded after title and abstract screening	929
Records excluded after full text screening	0
Results where full text could not be found	4
Articles identified through other sources	4
Number of full-text articles assessed for eligibility	36

Table S2 Treatment methods of 36 research articles selected for 1,2,3-Tricholoropropane treatment systematic review.

Treatment Technology	Number of papers	Percentage %
Bioremediation (bacteria catalyzed)	13	36
Reduction with zinc, iron or both	8	22
Granulated Activated Carbon (GAC)	4	11
Persulfate oxidation	4	11
Fenton's treatment (Iron catalyzed hydrogen peroxide)	2	6
Ammonia Treatment	1	3
Hydrogen-assisted dichlorination with Pt-Sn Catalyst	1	3
Sonolysis	1	3
Reviews (non-systematic)	4	11

*Note: Total does not add up to 36 as some papers fall into multiple categories.

Table S3 Summary of research using various species of bacteria to dechlorinate 1,2,3-Tricholoropropane ordered by publication date.

Author, date	Bacteria name	Anaerobic or Aerobic	*Location isolated	Recom-binant?	TCP degrading enzyme	[TCP] all in µM	Degradation kinetics Kcat/km	Products of degradation (if stated)
Bosma and Janssen, 1998	Methylosinus trichosporium	Aerobic (cometabolic)	National Collection of Industrial and Marine Bacteria, Aberdeen, UK	No	methane monooxygenase - cometabolism	50 µM	kcat/km = 0.07 - 1.03 mL/mg-min	Chloride, 2-Chloro-1-propanol, 1,3-Dichloro-1-propanol, 2, 3-Dichloro-1-propanol
Bosma et al., 1999	Agrobacterium radiobacter	Aerobic	none stated	Yes	haloalkane dehalogenase	1600 µM	0.7mM/25days	none listed
Bosma et al., 2002	Rhodococcus	Aerobic	none stated	Yes	haloalkane dehalogenase	1000 µM	0.28/sec	2,3-dichloro-1-propanol
Monincová et al., 2007	Sphingobium japonicum	Aerobic	Soil bacterium	No	Haloalkane dehalogenase LinB	None stated	kcat/Km = 0.068 s^{-1} M^{-1}	2,3-dichloropropan-1-ol
Pavlova et al., 2009	Rhodococcus rhodochrous	Aerobic	none stated	Yes	DhaA mutant haloalkane dehalogenase	None stated	Kcat/Km = 1,050/sec-M	2,3-dichloropropane-1-ol (DCL)
Yan et al., 2009	Dehalogenimonas lykanthroporepellens BL-DC-8 and BL-DC-9	Anaerobic	Superfund site - Baton Rouge, LA	No	none stated	500 µM	None stated	Allyl chloride
Li and Shao, 2014	Alcanivorax	Aerobic	"marine environments" - surface water of arctic	No	haloalkane dehalogenase (DadB)	None stated	5.6 ± 0.6 ng/mg-sec	None stated
Samin et al., 2014	Pseudomonas putida	Aerobic	none stated	Yes	Dehalogenase DhaA31	330 µM	kcat/km = 1.050/M-sec	chloride
Gong et al., 2017	Psudomonas putida	Aerobic	none stated	Yes	DhaA31	200 µM	kcat/km = 1050/sec-M	chloride
Schmitt et al., 2017	Dehalogenimonias	Anaerobic	none stated	No	None stated	16,000 µM	0.407 mg/L/Day	None stated
Wang and Chu, 2017	Propane oxidizing bacteria (PrOB)	Aerobic	none stated	No	propane monoxygenase	4500	9.7 ± 0.7 mg TCP/(mg protein)/hour	Chloride
Vannelli et al., 1990	Nitrosomonas europaea	Aerobic	none	No	ammonia monooxygenase	10 -15 µM	0.9 µmol/hr-g	None stated
Kurumbang et al., 2014	Escherichia coli	Aerobic	none	Yes	DhaA31	2 mM	kcat/Km = 1050 s^{-1} M^{-1}	Glycerol

Table S4 1,2,3-Tricholoropropane reduction with Zero valent Iron or Zinc. Degradation rate constants normalized for surface area or percent reduction for comparison.

Study	Title	Treatment	$[TCP]_{time=0}$	Surface area normalized degradation rate constant K_{SA} or percent reduction
Vikesland et al., 2003	Longevity of Granular Iron in Groundwater Treatment Processes: Solution Composition Effects on Reduction of Organohalides and Nitroaromatic Compounds	ZVI	100 µM	20%
Sarathy et al., 2010	Degradation of 1,2,3-Trichloropropane (TCP): Hydrolysis, Elimination, and Reduction by Iron and Zinc	ZVI* ZVZ	100-280 µM 100 µM	ZVI: insignificant rates K_{SA} = 10^{-4} L m^{-2} h^{-1} ZVZ: 10^{-3} - 10^{-2} L m^{-2} h^{-1}
Tratnyek et al., 2010	Report for SERDP: Prospects for Remediation of 1,2,3-Trichloropropane by Natural and Engineered Abiotic Degradation Reactions	Batch studies ZVI ZVZ	150 µM	ZVI: Little to no degradation ZVZ: K_{SA} = 10^{-3} L m^{-2} h^{-1}
Salter-Blanc & Tratnyek, 2011	Effects of Solution Chemistry on the Dechlorination of 1,2,3-Trichloropropane by Zero-Valent Zinc	ZVZ	30µM	ZVZ: 10^{-3} - 10^{-2} L m^{-2} h^{-1}
Salter-Blanc et al., 2012	Evaluation of Zerovalent Zinc for Treatment of 1,2,3-Trichloropropane-Contaminated Groundwater: Laboratory and Field Assessment	ZVZ	30µM	ZVZ (grade 1210) with and without sand K_{SA} 2.08-3.32 x 10^{-3} Lm^{-2} h^{-1}
Hui et al., 2015	Comparison of 1,2,3-Trichloropropane reduction and oxidation by nanoscale zero-valent iron, zinc and activated persulfate	ZVI – from green tea ZVZ	10^5 µM 10^5 µM	Negligible 100%
Lapeyrouse et al., 2019	Remediation of Chlorinated Alkanes by Vitamin B12 and Zero-Valent Iron	Vitamin B-12 and ZVI	12, 270 µM	Kobs = 0.287 day^{-1}
Torralba-Sanchez et al., 2020	Reduction of 1,2,3-trichloropropane (TCP): pathways and mechanisms from computational chemistry calculations	Batch experiments with ZVZ	None stated	k_{SA} = 5.44 ± 0.56 x 10^{-4} (Lg^{-1} m^{-2})

*nanoscale and construction grade ZVI used.

Table S5 Summary of GAC types used in each 1,2,3-tricholoropropane removal study.

Mital, 2013		**Harada, 2014**		**Babcock et al., 2018**		**Kurumbang et al., 2014**	
Columns: 0.7cm inside diameter and 10.3 cm depth of carbon		Columns: 4.76 mm inside diameter and 2.00 cm depth of carbon.		Columns: 4.76 mm inside diameter and 2.00 cm depth of carbon.		None specified	
GAC Name	Composition	GAC Name	Composition	GAC Name	Composition	GAC Name	Composit-ion
Filtrasorb 400 (F400)	Calgon Virgin bituminous coal, reagglomerated	CF400 12x40	Calgon coal-based carbon	CF400 12x40	Calgon coal-based carbon	GAC 400; Norit Americas Inc.	Fresh bitumin ous-based coal
OLC 12x40	Virgin coconut, direct activated	COLC 12x40	Calgon Coconut Shell Carbon	COLC 12x40	Calgon Coconut Shell Carbon		
OLC 12x30	Virgin coconut, direct activated	JCL 8x30*	Jacobi direct activated coal-based carbon	JCL 8x30*	Jacobi direct activated coal-based carbon		
CMR Lincave	Coconut, direct activated	JCS 12x40	Jacobi Coconut shell carbon	JCS 12x40	Jacobi Coconut shell carbon		
Aquacarb 1230CX	Coconut Siemans	SC 12x30	Siemen's coconut shell carbon	SC 12x30	Siemen's coconut shell carbon		
		SCX 12x30	Siemens enhanced coconut shell carbon	SCX 12x30	Siemens enhanced coconut shell carbon		

*Currently in use by BWS (Board of Water Supply) in Hawaii

Table S6 1,2,3-Tricholoropropane removal amount for most efficient GAC in each location or study normalized to column volume

Author, date	Well Location	Optimal GAC	Composition	Ave TCP Influent conc ng/L	Effluent conc ng/L	% TCP reduction	ng sorbate/kg sorbent at 1% TCP breakthrough
Babcock et al., 2017	Kunia (K)	SCX	Siemens enhanced coconut shell carbon	800	5	99.4	255
	Mililani (M)	CF400	Calgon coal-based carbon	2200	5	99.8	677
	Waipahu (W)	SC	Siemen's coconut shell carbon	600	5	99.2	208
Harada, 2014	Kunia (K)	SC	Siemen's coconut shell carbon	805	8.05	99	258
	Mililani (M)	CF400	Calgon Coconut Shell Carbon	2,220	22.2	99	676
	Waipahu (W)	SCX	Siemens enhanced coconut shell carbon	576	5.76	99	208
Mital, 2014	Livingston	F400	Virgin bituminous coal reagglomerat-ed	200	5	97.5	Not enough information
Kempisty et al., 2020	Cincinnati, OH	GAC 400	Fresh bituminous-based coal	500	0.5	90	Not enough information

Table S7 Most effective parameters and by products for Fenton's process studies

Authors, date	Title	Initial TCP Conc	Optimal Iron ion 2+ or 3+	Contact Time	% Reduc-tion	Optimal Molar ratios	By-products
Hunter, 1997	Fenton's treatment of 1,2,3-trichloropropane: Chemical reaction byproducts, pathway, and kinetics	150 ppm	Fe^{2+}	14 days	95%	TCP: H_2O_2:Fe^{2+} 1:10:10	1,3 dichloropropanone; chloroacetic acid, formic acid
Khan et al., 2009	Effects of iron type in Fenton reaction on mineralization and biodegradability enhancement of hazardous organic compounds	20 ppm	Fe^{2+}	(0.125 days) 180min	90%	TCP: H_2O_2:Fe^{2+} 1:10:10	1,3-dichloro-2-propanone, 2,3-dichloro-1-propene, isopropanol, and propionic aldehyde

Table S8 Key parameters from studies focusing on persulfate oxidation.

Author, date	Title	Initial TCP Conc	Rate constant	Activation method	By-products
Li et al., 2019	In Situ Persulfate Oxidation of 1,2,3-Trichloropropane in Groundwater of North China Plain	28.76 mg/L	61.4% reduction efficiency	Ferrous Sulfate (Fe2+) and citric acid	None stated
Li et al., 2015	Comparison of 1,2,3-Trichloropropane reduction and oxidation by nanoscale zero-valent iron, zinc and activated persulfate	100 mg/L	50 % reduction in 24 hours		
Huang et al., 2005	Degradation of volatile organic compounds with thermally activated persulfate oxidation	None stated	Little to no reduction (<20% in 72 hours)	Heat	None Stated
Tratnyek et al., 2010	Report: Prospects for Remediation of 1,2,3-Trichloropropane by Natural and Engineered Abiotic Degradation Reactions	150 µM	2.7 x 10^6 M-1 s-1	Heat	None – complete mineralization

Table S9 Key parameters from sonolysis study

Author, date	Initial TCP Concentration	Degradation rate at 10°C	Byproducts
Lim et al., 2007	100 mg/L	0.00960 min^{-1}	None stated

Table S10 Comparison of separation based and elimination-based treatments for water contaminated with TCP

Process	Separation or elimination based	Benefits	Shortcomings
Bioremediation (bacteria catalyzed)	Elimination	Enzymatically breaks down TCP	Can require the addition of a carbon source (such as propane) or lactate as a hydrogen source Slow degradation rates Toxic intermediates may accumulate
Reduction with Iron	Elimination	N/A	Negligible degradation, incomplete reduction allows for accumulation of intermediates
Reduction with Zinc	Elimination	Bench tests show promising degradation rates No undesirable by products	More groundwater level testing in the field is needed. Inhibited by alkaline groundwater
Granulated Activated Carbon (GAC)	Separation	Proven Technology Operationally simple	Separation based does not degrade TCP Costly due to a low sorption affinity of TCP-GAC requiring periodic media replacement Site-level testing with contaminated groundwater needed to optimize efficiency
Fenton's treatment (Iron catalyzed hydrogen peroxide)	Elimination	Limited experimental data	Partially chlorinated byproducts produced
Hydrogen-assisted dechlorination with Pt-Sn Catalyst	Elimination	Limited experimental data	Limited experimental data
Sonolysis	Elimination	No reagents required	Limited experimental data Requires large amount of energy Lack of research on if incomplete mineralization leads to accumulation of byproducts

Table S11: Papers with reported pH information grouped by treatment type.

Author (Publication Date)	Title	Treatment method or Review	Experimental pH conditions
Coyle et al. (2017)	Use of dilute ammonia gas for treatment of 1,2,3-trichloropropane and explosives-contaminated soils	Ammonia	pH increased from 8-10
Bosma and Janssen (1998)	Conversion of chlorinated propanes by Methylosinus trichosporium OB3b expressing soluble methane monooxygenase	Bioremediation	buffer solution pH6.9
Bosma et al. (1999)	Utilization of trihalogenated propanes by Agrobacterium radiobacter AD1 through heterologous expression of the haloalkane dehalogenase from Rhodococcus sp. strain M15-3.	Bioremediation	buffer solution pH8.2-9.4
Bosma et al. (2002)	Biodegradation of 1,2,3-Trichloropropane through Directed Evolution and Heterologous Expression of a Haloalkane Dehalogenase Gene	Bioremediation	buffer solution pH9.4
Gong et al. (2017)	Combinatorial metabolic engineering of Pseudomonas putida KT2440 for efficient mineralization of 1,2,3-trichloropropane.	Bioremediation	pH7.2
Kurumbang et al. (2014)	Computer-Assisted Engineering of the Synthetic Pathway for Biodegradation of a Toxic Persistent Pollutant	Bioremediation	pH8.5
Li and Shao (2014)	Biochemical characterization of a haloalkane dehalogenase DadB from Alcanivorax dieselolei B-5.	Bioremediation	pH 5.5-pH 6.0 and pH 8.0–pH 9.0
Monincová et al. (2007)	Weak activity of haloalkane dehalogenase LinB with 1,2,3-trichloropropane revealed by X-Ray crystallography and microcalorimetry	Bioremediation	pH 8.75
Pavlova et al. (2009)	Redesigning dehalogenase access tunnels as a strategy for degrading an anthropogenic substrate	Bioremediation	buffer solution pH8.6
Samin and Janssen (2012)	Transformation and biodegradation of 1,2,3-trichloropropane (TCP)	Bioremediation	n/a
Samin et al. (2014)	A Pseudomonas putida strain genetically engineered for 1,2,3-trichloropropane bioremediation	Bioremediation	pH 7
Schmitt et al. (2017)	Optimization and validation of enhanced biological reduction of 1,2,3-trichloropropane in groundwater	Bioremediation	pH 7-9
Vannelli et al. (1990)	Degradation of Halogenated Aliphatic Compounds by the Ammonia-Oxidizing Bacterium Nitrosomonas europaea	Bioremediation	n/a
Wang and Chu (2017)	Cometabolic biodegradation of 1,2,3-trichloropropane by propane-oxidizing bacteria	Bioremediation	n/a
Yan et al. (2009)	Isolation of novel bacteria within the Chloroflexi capable of reductive dechlorination of 1,2,3-trichloropropane	Bioremediation	7.0–7.5

Hunter (1997)	Fenton's treatment of 1,2,3-trichloropropane: Chemical reaction byproducts, pathway, and kinetics	Fenton reaction	pH3
Khan et al. (2009)	Effects of iron type in Fenton reaction on mineralization and biodegradability enhancement of hazardous organic compounds	Fenton reaction	pH 2-4
Harada (2014)	Comparative evaluation of six different granular activated carbon for TCP removal using rapid small-scale column test	GAC	n/a
Mital, J. (2014)	Granular Activated Carbon Treatment of 1, 2, 3-Trichloropropane	GAC	pH7.9-8
Babcock et al. (2018)	Adsorption of 1,2,3-Trichloropropane (TCP) to meet a MCL of 5 ppt	GAC	n/a
Kempisty et al. (2020)	Granular activated carbon adsorption of carcinogenic volatile organic compounds at low influent concentrations	GAC	pH7-7.8
Early et al. (2000)	Hydrogen-assisted 1,2,3-trichloropropane dechlorination on supported Pt-Sn catalysts	Hydrogen assisted dechlorination	n/a
Huang et al. (2005)	Degradation of volatile organic compounds with thermally activated persulfate oxidation	Persulfate	pH2.1-2.5
Li et al. (2019)	In Situ Persulfate Oxidation of 1,2,3-Trichloropropane in Groundwater of North China Plain	Persulfate	2.52–3.01
Tratnyek et al. (2008)	Fate and remediation of 1, 2, 3-trichloropropane.	Review	n/a
Merrill et al. (2019)	Development and Validation of Technologies for Remediation of 1,2,3-Trichloropropane in Groundwater	Review	pH 7-9 optimal (Schmidt et al. 2017)
Porter and Mackey (2018)	Preparing for Change: TCP Overview and Treatment Considerations	Review	n/a
Lim et al. (2007)	Sonolysis of chlorinated compounds in aqueous solution	Sonolysis	pH drops to 3
Klausen et al. (2003)	Longevity of granular iron in groundwater treatment processes: Solution composition effects on reduction of organohalides and nitroaromatic compounds	ZVI	pH 9.3 drops initially and then rebounds
Lapeyrouse et al. (2019)	Remediation of Chlorinated Alkanes by Vitamin B-12 and Zero-Valent Iron	ZVI	n/a
Sarathy et al. (2010)	Degradation of 1,2,3-Trichloropropane (TCP): Hydrolysis, elimination, and reduction by iron and zinc	ZVI, ZVZ	pH 9.2 and 11
Tratnyek et al. (2010b)	Prospects for Remediation of 1, 2, 3-Trichloropropane by Natural and Engineered Abiotic Degradation Reactions.	ZVI, ZVZ, Persulfate	pH above 10 or below 8
Li et al. (2015)	Comparison of 1,2,3-Trichloropropane reduction and oxidation by nanoscale zero-valent iron, zinc and activated persulfate	ZVI, ZVZ, Persulfate	n/a
Salter-Blanc and Tratnyek (2011)	Effects of solution chemistry on the dechlorination of 1,2,3- trichloropropane by zero-valent zinc	ZVZ	pH lowers than 8 and higher than 10

Salter-Blanc et al. (2012)	Evaluation of Zerovalent Zinc for Treatment of 1,2,3-Trichloropropane-Contaminated Groundwater: Laboratory and Field Assessment	ZVZ	pH<7 optimal
Torralba-Sanchez et al. (2020)	Reduction of 1,2,3-trichloropropane (TCP): pathways and mechanisms from computational chemistry calculations	ZVZ	n/a

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Appendix 2: Supplementary Information for Chapter 3

Supplementary Material: Using machine learning to predict 1,2,3-Trichloropropane contamination from legacy non-point source pollution of groundwater in California's Central Valley

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Table S1. Estimated mass loading ($\dot{m}$) of 1,2,3-trichloropropane (TCP) from historical Pesticide Use Reports (PUR) (CDFA, 1973-1984).

Year	DD-mix (lbs)	DD-mix (kg)	Telone (lbs)	Telone (kg)	Total (kg)
1970	3,505,180.16	1,589,924.87	2,220,825.03	1,007,350.49	2,597,275.35
1971	0	0	1,957,898.99	888,089.10	888,089.10
1972	0	0	3,828,278.26	1,736,479.87	1,736,479.87
1973	0	0	2,132,493.65	967,284.00	967,284.00
1974	2,916,144.05	1,322,742.26	1,352,749.09	613,597.40	1,936,339.66
1975	3,176,865.86	1,441,003.83	1,365,511.60	619,386.38	2,060,390.21
1976	3,123,373.08	1,416,739.88	636,546.20	288,732.84	1,705,472.73
1977	3,647,289.67	1,654,384.73	778,596.70	353,165.94	2,007,550.68
1978	7,037,091.94	3,191,975.01	0.00	0.00	3,191,975.01
1979	12,314,782.30	5,585,897.93	0.00	0.00	5,585,897.93
1980	13,395,301.03	6,076,013.57	0.00	0.00	6,076,013.57
1981	16,426,393.77	7,450,895.74	0.00	0.00	7,450,895.74
1982	13,788,060.95	6,254,166.68	0.00	0.00	6,254,166.68
1983	12,806,589.31	5,808,978.11	0.00	0.00	5,808,978.11
1984	0.00	0.00	0.00	0.00	0.00
				Total minimum	888,089.10
				Total maximum	7,450,895.74

Table S2 Variables and constants used in 1,2,3-trichloropropane (TCP) mass balance equation

Symbol	Description	Value	Unit	Source
$\dot{m}$	Mass flux	144,227,025.38	grams/year	Estimated from historical PUR documents
D_a	Diffusion Coefficient of TCP in air	229.1	meters$^{2/}$year	Environmental Protection Agency's calculator for the Estimated Diffusion Coefficients in air using the Hayduk and Laudie method 0.0726 cm^2/sec converted to m^2/yr (EPA, 2021)
A	Area	155,376,437.84	meters^2	Estimated from historical PUR documents
C_a	TCP Concentration	1.32E^{-09}	g/m^3	Initial calculated from $C_{a0} = \dot{m}/V_t * R_a$
Z_1	Upper boundary topsoil depth	0.5	meters	Assumed 0.5 meters
Z_2	Lower boundary topsoil depth	5	meters	Assumed 5 meters
V	Volume of the soil layer	77,688,218.92	meters^3	Product of area and depth (Z_2-Z_1)
n	Porosity	0.5	g/m^3	Estimated
Θ_a	Volumetric air constant	0.5	Unitless	Assumed 0.5
Θ_w	Volumetric water constant	0.5	Unitless	Assumed 0.5
KH'	Dimensionless Henry's constant	0.014029605	Unitless	Calculated from KH/RT
Pb	Bulk density of soil	1.4E^{06}	g/m^3	Assumed 1.4 g/cm^3 converted to g/m^3
K_d	Soil adsorption coefficient	1.00E^{-08}	m^3/g	Volume water per gram of sediment calculated from Kd = f_{OC} x K_{OC}

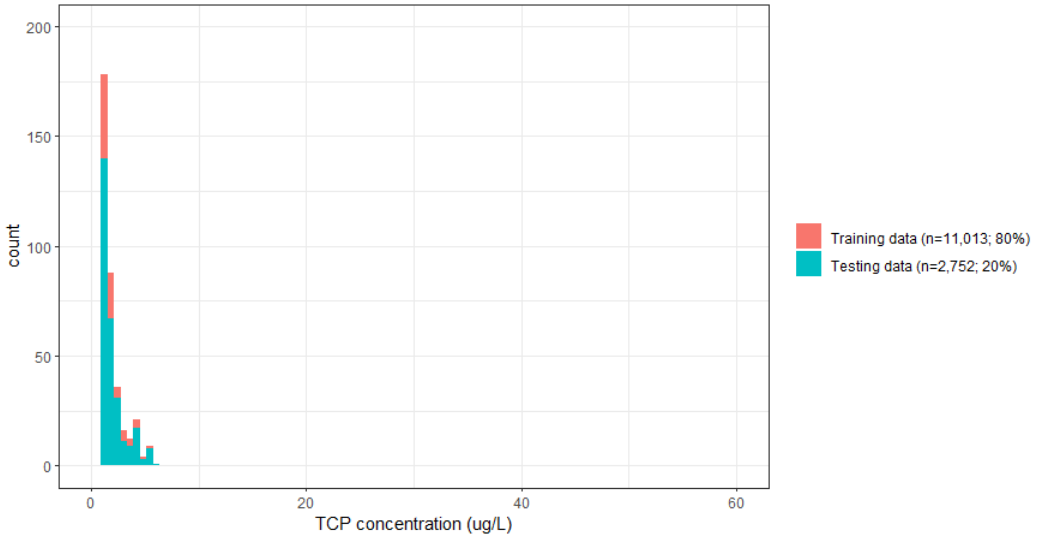
Table S3. Workflow of geospatial and statistical analysis of 1,2,3-trichloropropane (TCP) contamination and explanatory variables. Steps from left to right and top to bottom.

DATA COLLECTION AND ASSEMBLY	**COLLECT CONTAMINATION POINT DATA** California Water Boards GAMA website. Export all data from 20 Central Valley CA. for all years to Excel and save as csv file: TCP: (13,747 points)	**COLLECT SPATIAL RASTER DATA** Land use classification and Irrigation UC Davis CAML data; Hydrologic soil class USGS data; Soil drainage class USGS data; Nitrate USGS data, Dissolved oxygen USGS data; Groundwater age SWRCB data; Precipitation PRISM climate group data. See Table 1 for web links.	**SPATIAL DATA ASSEMBLY** **ACTION:** Add csv and raster, data to Arc GIS Pro version 2.8.2 and match map coordinate system to CAML layers **ArcGIS TOOL:** Project
GEOSPATIAL DATA PROCESSING	**ACTION:** Define study area using 1945 land use **ArcGIS TOOLS:** 'Raster to polygon'; 'Dissolve (for study area outline)	**ACTION:** Clip all data layers with study area outline **ArcGIS TOOL:** 'Clip raster'	**ACTION:** Obtain mean well point data mean concentration by well ID **ArcGIS TOOL:** 'Dissolve'	**ACTION:** Add a 500-meter circular buffer zone around TCP well point data (repeat for 1000, and 1500 meters) **ArcGIS TOOL:** 'Buffer'	**ACTION:** Remove outlier TCP well data. Point considered outlier if 3 or more standard deviations from mean (calculated in Excel) **ArcGIS TOOL:** 'Table to excel'
GEOSPATIAL ANALYSIS	**ACTION:** Calculate majority land use, soil type, age, surrounding three buffer zones (500, 1000, 1500 meters) **ArcGIS TOOL:** 'Zonal Statistics as table' by majority	**ACTION:** Join each zonal statistics table to dissolved and buffered TCP layer. Repeat three buffer zones (500, 1000, 1500 meters) **ArcGIS TOOL:** 'Join'	**ACTION:** Export TCP explanatory data layer to excel **ArcGIS TOOL:** 'Table to Excel'		
MODELING	**ACTION:** Install 'caret' package in R Studio. Read TCP explanatory variable layers (as csv files) for different buffer zones to R.	**ACTION:** Log_{10} transform TCP data and replace zeros with half detection limit (0.0025) **R 'dplyr' function:** Mutate	**ACTION:** Randomly partition data into (80%) train and (20%) test datasets **R 'caret' function:** createDataPartition()	**ACTION:** Train model and use to predict on to train and test data for machine learning models in the caret package: rpart2, rf, and gbm **R 'caret' function:** train() and predict()	
MODEL PROJECTION	**ACTION:** Export explanatory layers from Arc GIS Pro to **ArcGIS TOOL:** Export Raster (as TIFF files)	**ACTION:** Install and load 'raster' package into R studio to stack all explanatory rasters into one TIFF layer **R 'raster' function:** stack()	**ACTION:** Rename layers in raster stack to match those in the model and convert raster stack to a data frame. Predict model to data frame and write raster to new tiff file. **R 'caret' function:** value(); predict();	**ACTION:** Import tiff file in Arc GIS Pro and reclassify values **ArcGIS TOOL:** Reclassify	
MODEL MAP ANALYSIS	**ACTION:** Reclassify imported tiff file so that values are integers. Calculate area of each value category from the previous step. **ArcGIS TOOLS:** Reclassify; Tabulate area	**ACTION:** Import disadvantaged communities (DAC) geodatabase information from Cal EnviroScreen 4.0 (https://oehha.ca.gov/calenviroscreen/report/calenviroscreen-40). Clip layer to raster dimensions and dissolve boundaries. **ArcGIS TOOLS:** Clip; Dissolve		**ACTION:** Reclassify raster values to ranges. Then clip the raster by the DAC layer and use tabulate area tool to calculate areas of zones within DAC. **ArcGIS TOOL:** Reclassify. Tabulate area.	

Table S4: Summary statistics for 1,2,3-trichloropropane concentration data sets

	Training data TCP concentration (ug/L)	**Testing data TCP concentration (ug/L)**
Count	11,013	2,752
Minimum	0.0025	0.0025
1st Quartile	0.0025	0.0025
Median	0.0025	0.0025
Mean	0.2394	0.2149
3rd Quartile	0.0582	0.0575
Maximum	60.00	34.375
Standard deviation	2.15	1.71

a)



b)

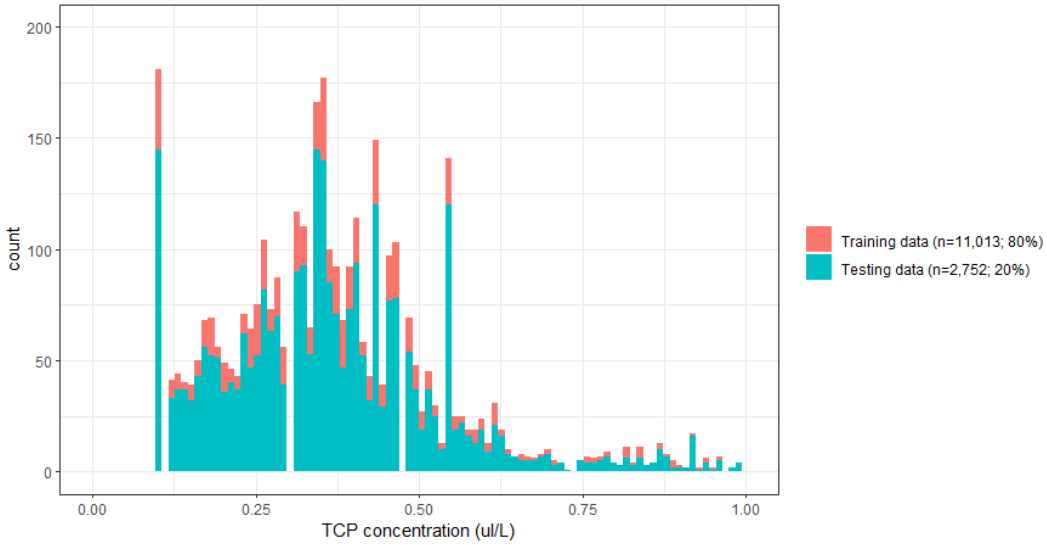


Figure S1: (a) Histogram of 1,2,3-trichloropropane (TCP) concentration well point data for training and testing models Concentration is in or ppb (µg/L). Plot (b) is the same as plot (a) but zooms in on concentrations up to 1 ppb.

Table S5 Land use categories key. Numbering from UC Davis CAML database (Harter, 2017)

Code	Land use	Code	Land use
1	Urban	8	Field crops
2	Native vegetation	9	Corn, sorghum, sudangrass
3	Pasture	10	Grain
4	Barren	11	Alfalfa
5	Water	12	Semi Agricultural
6	Citrus and subtropical	13	Truck, Nursery, and Berry Crops
7	Deciduous fruit and nut	14	Rice
		15	Vineyards

Table S6 Hydrologic soil groups. Group D soils may be further categorized as: A/D, B/D, or C/D where the first letter is the soil's group under drained conditions and the second when wet (USDA, 2019).

Group	Characteristics
A	Soils with a high infiltration rate and low runoff with deep well-drained sands.
B	Soils have a moderate infiltration rate with deep well-drained soils.
C	Soils have a slow infiltration rate and may have a layer that impedes the downward movement of water.
D	Soils have a very slow infiltration rate and high runoff potential due to a high water table or a surface clay layer.
A/D	Soils have very slow infiltration rates when the water table is high but high infiltration and low runoff rates if drained.
B/D	Soils have a very slow infiltration rate with a high water table but a moderate rate of infiltration and runoff if drained.
C/D	Soils have very slow infiltration rates when wet and drained.

Table S7 Soil Drainage Class. The eight values of drainage class are defined by the NRCS Soil Survey Manual (USDA Soil Science Division Staff, 2017).

Value. Class	Description
0. Excessively drained	Water is removed very rapidly. The occurrence of internal free water commonly is very rare or very deep. The soils are commonly coarse-textured and have very high hydraulic conductivity or are very shallow.
1. Somewhat excessively drained	Water is removed from the soil rapidly. Internal free water occurrence commonly is very rare or very deep. The soils are commonly coarse-textured and have high saturated hydraulic conductivity or are very shallow.
2. Well drained	Water is removed from the soil readily but not rapidly. Internal free water occurrence commonly is deep or very deep; annual duration is not specified. Water is available to plants throughout most of the growing season in humid regions. Wetness does not inhibit the growth of roots for significant periods during most growing seasons. The soils are mainly free of the deep to redoximorphic features that are related to wetness
3. Moderately well drained	Water is removed from the soil somewhat slowly during some periods of the year. Internal free water occurrence commonly is moderately deep and transitory through permanent. The soils are wet for only a short time within the rooting depth during the growing season, but long enough that most mesophytic crops are affected. They commonly have a moderately low or lower saturated hydraulic conductivity in a layer within the upper 1 m, periodically receive high rainfall, or both.
4. Somewhat poorly drained	Water is removed slowly so that the soil is wet at a shallow depth for significant periods during the growing season. The occurrence of internal free water commonly is shallow to moderately deep and transitory to permanent. Wetness markedly restricts the growth of mesophytic crops, unless artificial drainage is provided. The soils commonly have one or more of the following characteristics: low or very low saturated hydraulic conductivity, a high water table, additional water from seepage, or nearly continuous rainfall.
5. Poorly drained	Water is removed so slowly that the soil is wet at shallow depths periodically during the growing season or remains wet for long periods. The occurrence of internal free water is shallow or very shallow and common or persistent. Free water is commonly at or near the surface long enough during the growing season so that most mesophytic crops cannot be grown unless the soil is artificially drained. The soil, however, is not continuously wet directly below plow depth. Free water at shallow depths is usually present. This water table is commonly the result of low or very low saturated hydraulic conductivity of nearly continuous rainfall, or of a combination of these.
6. Very poorly drained	Water is removed from the soil so slowly that free water remains at or very near the ground surface during much of the growing season. The occurrence of internal free water is very shallow and persistent or permanent. Unless the soil is artificially drained, most mesophytic crops cannot be grown. The soils are commonly level or depressed and frequently ponded. If rainfall is high or nearly continuous, slope gradients may be greater.
7. Subaqueous Soils	These soils are under the surface of a body of water. (There are only a few of these in the entire dataset.)

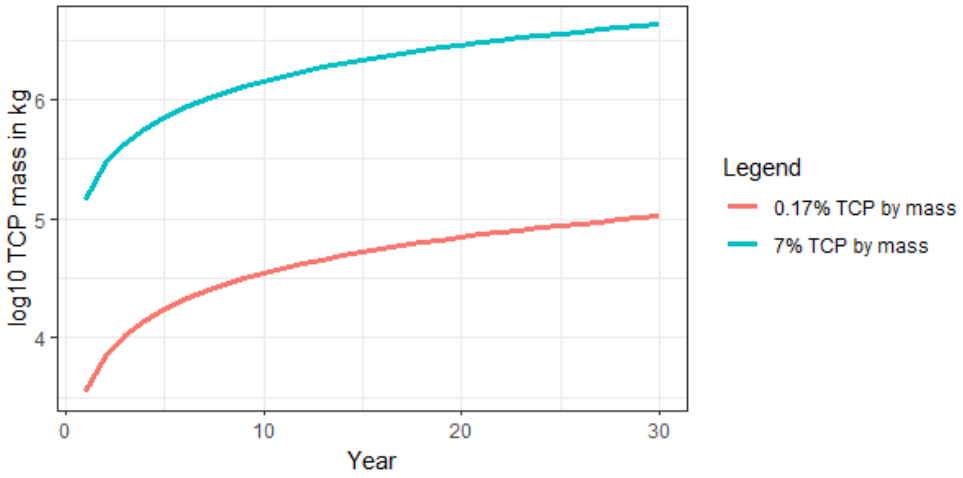


Figure S2 Mass accumulation of 1,2,3-Trichloroproane (TCP) in groundwater over 30 years.

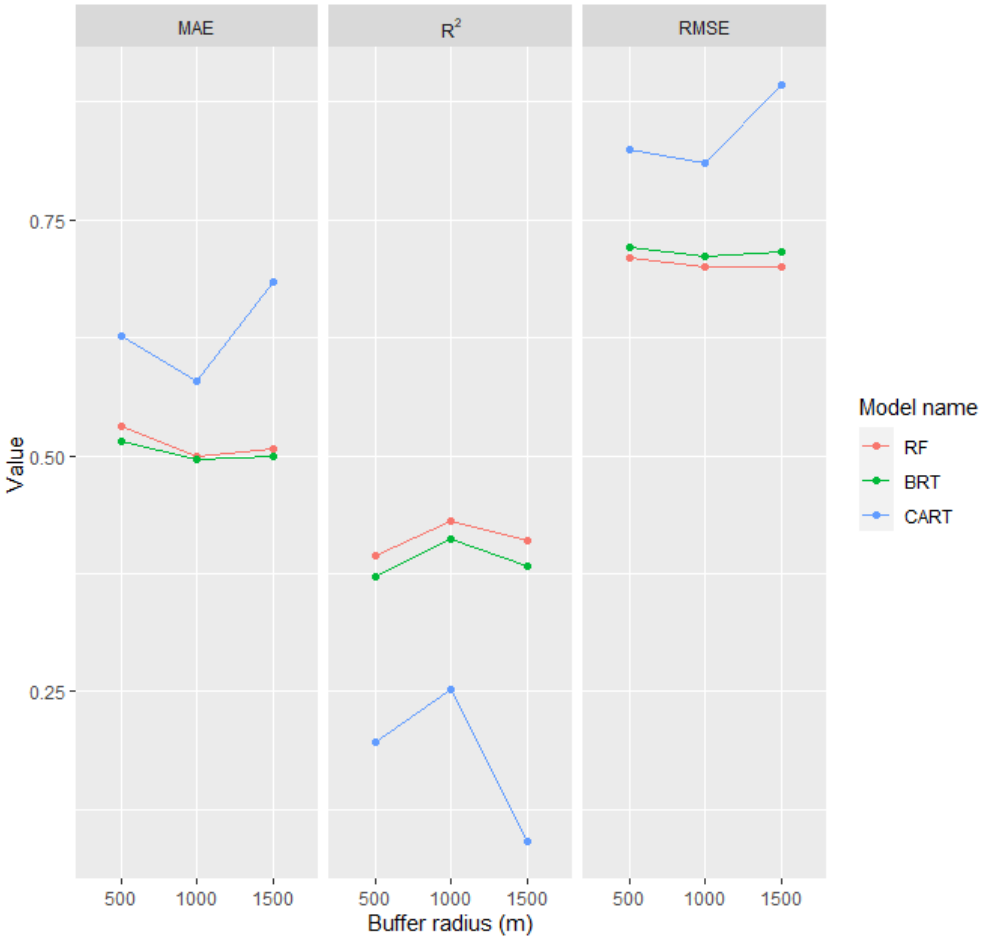


Figure S3 Comparison of the mean predictive performance MAE (Mean Absolute Error), R^2 (coefficient of determination), and RMSE (Root Mean Squared Error) for CART (classification and regression tree), RF (Random Forest), and BRT (boosted regression tree) models based on the testing data. Error metrics are based on three different circular buffer areas: 500-meter radius (0.196 km^2), 1000-meter radius (0.785 km^2), and 1500-meter radius (1.77 km^2)

Table S8 Performance metrics for training and testing data for model predictions and EDF bias-corrected predictions for three tested models with a 1000-meter buffer zone surrounding well points. Units of MAE and RMSE are log(µg/L).

	Training data (n=10,652)						Testing data (n=2,662)					
Model	**MAE**	**MAE Bias Corrected**	**RMSE**	**RMSE Bias Corrected**	**R^2**	**R^2 Bias Corrected**	**MAE**	**MAE Bias Corrected**	**RMSE**	**RMSE Bias Corrected**	**R^2**	**R^2 Bias Corrected**
CART	0.74	0.71	0.88	1.1	0.038	0.026	0.76	0.74	0.91	1.2	0.029	0.020
RF	0.24	0.089	0.32	0.20	0.92	0.95	0.51	0.43	0.70	0.72	0.42	0.44
BRT	0.22	0.12	0.30	0.24	0.90	0.93	0.50	0.44	0.72	0.76	0.40	0.41

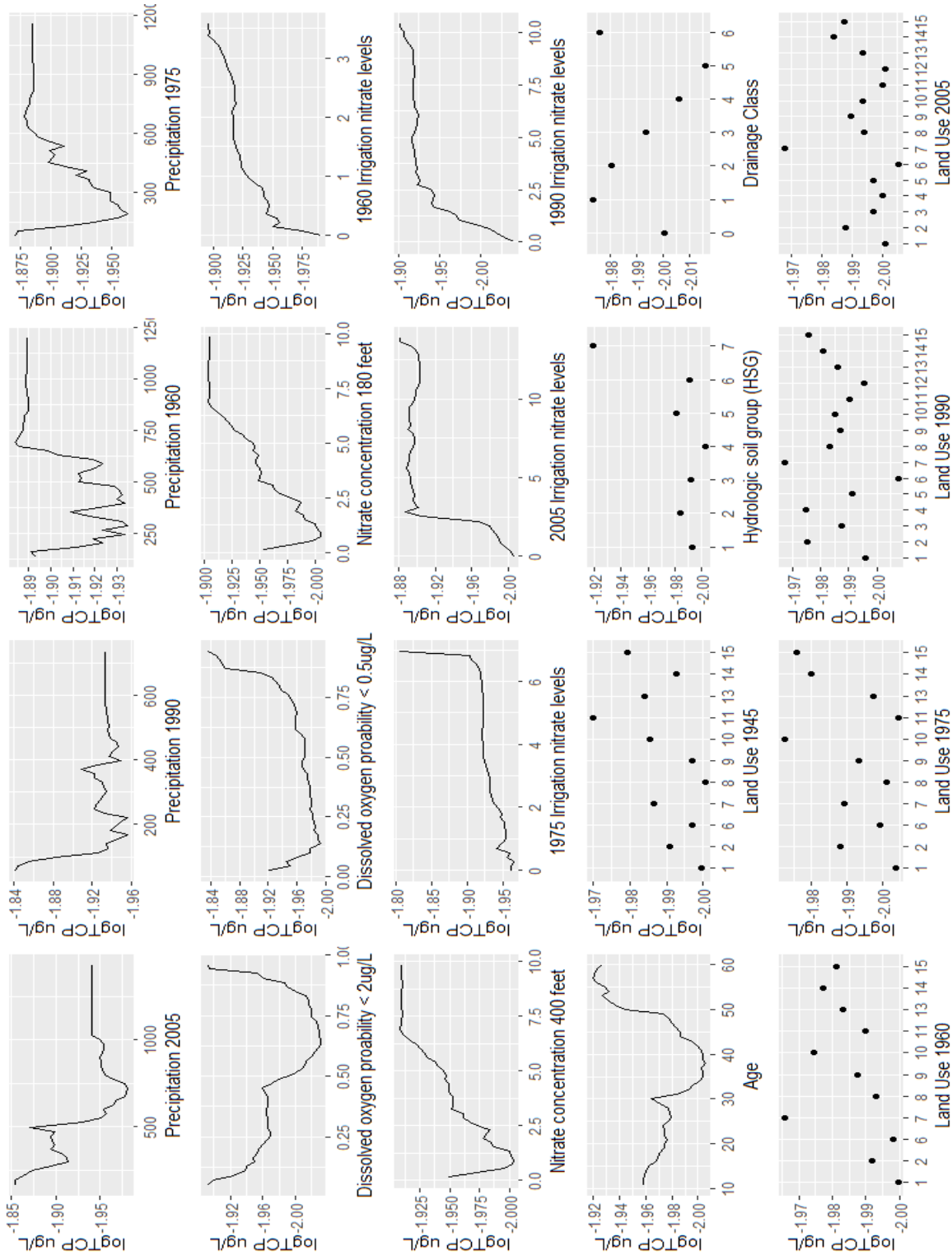


Figure S4: Partial dependence plots for the predictor variables from the Random Forest (RF) model in order of decreasing importance.

Table S9: Median 1,2,3-trichloropropane (TCP) concentration (micrograms/liter) for different land use categories using multiple historical land use years. Data from Groundwater Ambient Monitoring & Assessment Program (GAMA) and California Augmented Multisource Landcover Map (CAML) land-use layers. Compiled in ArcGIS Pro 2.8.2. The median was calculated and sorted using R v. 4.1.3.

Land Use	1945	1960	1975	2005
Alfalfa	0.0071429	0.0039444	0	0.0025
Barren	no data	no data	no data	0.00125
Citrus and subtropical	0	0	0	0.00125
Corn, sorghum, and sudangrass	0.005	0.005	0.0008333	0.0019375
Deciduous fruit and nut	0.00475	0	0	0.0023611
Field crops	0.005	0.005	0.004	0.0029
Grain	0.0008979	0.0033333	0.005	0
Native vegetation	0	0	0	0.0021429
Pasture	no data	no data	no data	0
Rice	0	0	0	0
Semiagricultural	no data	no data	no data	0.006
Truck, Nursery, and Berry Crops	0	0	0.0006571	0
Urban	0	0	0	0
Vineyards	0.0212535	0.0075	0.009	0.006

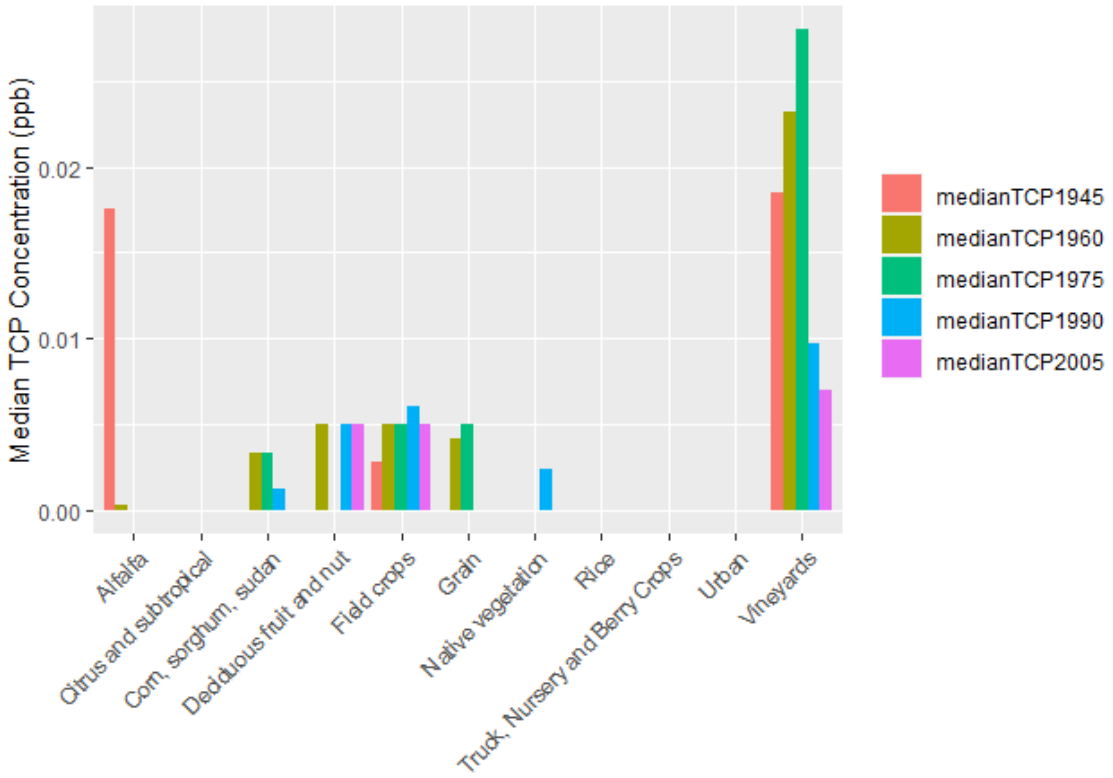


Figure S5: Historical Land Use Designation and Median 1,2,3-trichloropropane (TCP) Concentration in a 1000-meter circular buffer around groundwater well points. Well data from Groundwater Ambient Monitoring and Assessment in the Central California Aquifer, California, USA (GAMA, 2021).

Table S10: Areas and percent of the total study area (52,825 km^2) using Random Forest model associated with 1,2,3-trichloropropane (TCP) concentration within given ranges and percent also occurring in Disadvantaged Communities (DACs).

TCP Concentration (µg/L)	Area (km^2)	% of the total study area	% in DACs
0-0.1	6,991	15	42
0.1-0.2	26,676	56	43
0.2-0.3	10,706	23	70
0.3-0.4	2,367	5	75
0.4-0.862	586	1	73

Supplement References

California Department of Food and Agriculture (CDFA). (1970-1984). Pesticide Use Reports (PUR). Retrieved from the California State Library Archives, California, USA as hard copies.

United States Environmental Protection Agency (USEPA). (2021). EPA On-line Tools for Site Assessment Calculation. Retrieved from https://www3.epa.gov/ceampubl/learn2model/part-two/onsite/estdiffusion-ext.html

Harter, T., Dzurella, K., Kourakos, G., Hollander, A., Bell, A., Santos, N., Hart, Q., King, A., Quinn, J., Lampinen, G. and Liptzin, D. (2017). Nitrogen fertilizer loading to groundwater in the Central Valley. Final report to the fertilizer research education program, Projects, pp.11-0301. Retrieved from https://www.cdfa.ca.gov/is/ffldrs/frep/pdfs/CompletedProjects/15-0454_partialFR-Harter.pdf

Appendix 3: Supplementary Information for Chapter 4

Table S1 pH, conductivity, Nitrate as NO_3, TOC, and TDS of source water samples (n=3).

Parameter	Method	Mean	Standard deviation
pH	Digital meter	7.49	0.077
pH with char a	Digital meter	7.49	0.008
Conductivity (us/cm)	Digital meter	251	5.37
Nitrate as NO_3 mg/L	EPA 300.0	9.20	0.40
TOC mg/L	SM 5310C	0.37	0.21
TDS mg/L	Digital meter	104	2.52
Temp C	Digital meter	21.5	0.00

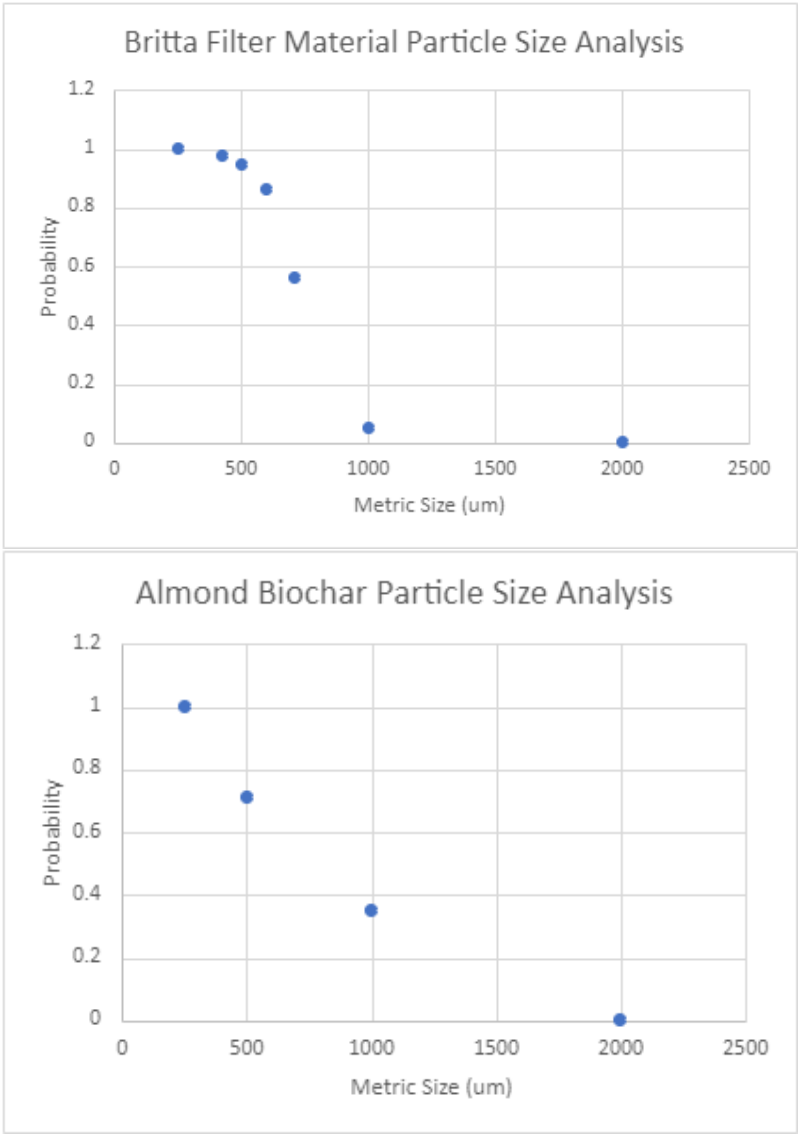
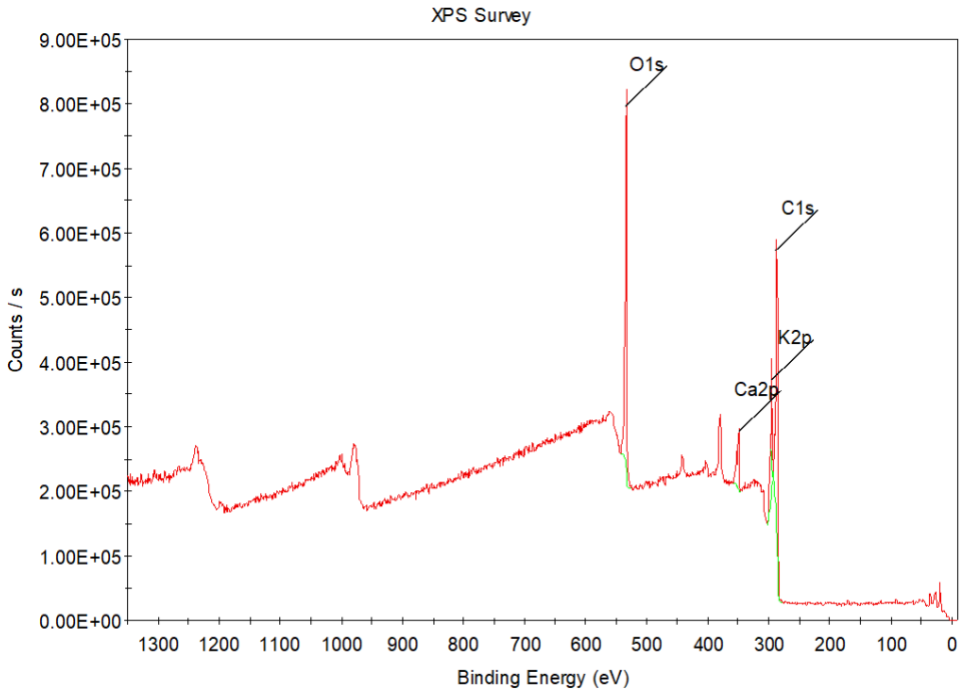


Figure S1 Particle Size Analysis for a) Brita Filter and b) Almond Biochar Samples

a.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8.00E+05
7.00E+05
6.00E+05
5.00E+05
4.00E+05
3.00E+05
2.00E+05
1.00E+05
0.00E+00
Counts / s
O1s
C1s
K2p
Ca2p
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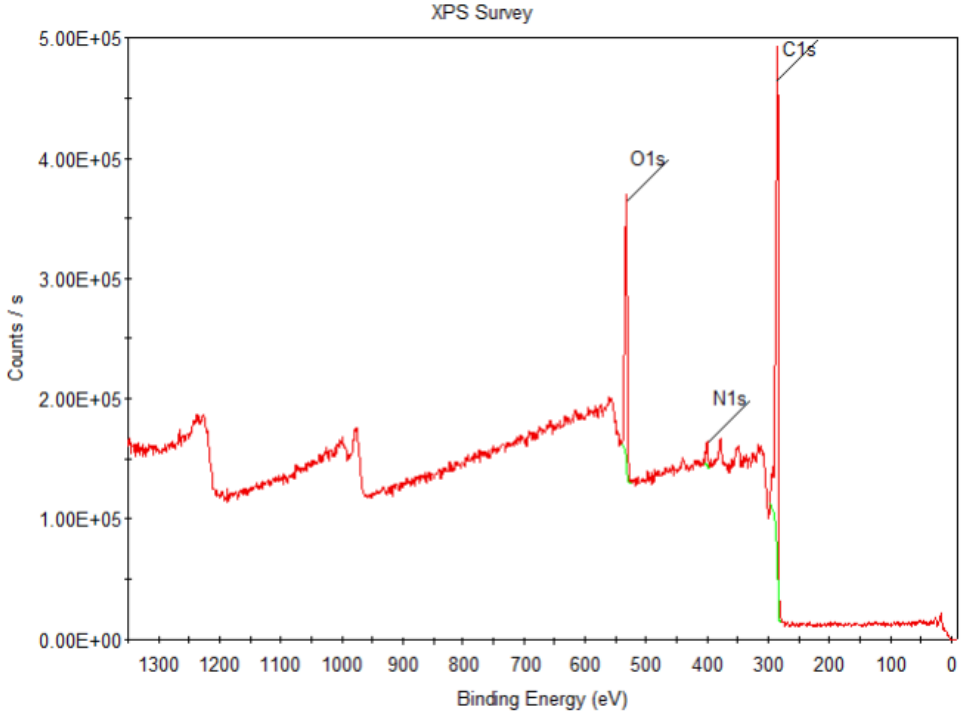
Binding Energy (eV)

b.


XPS Survey
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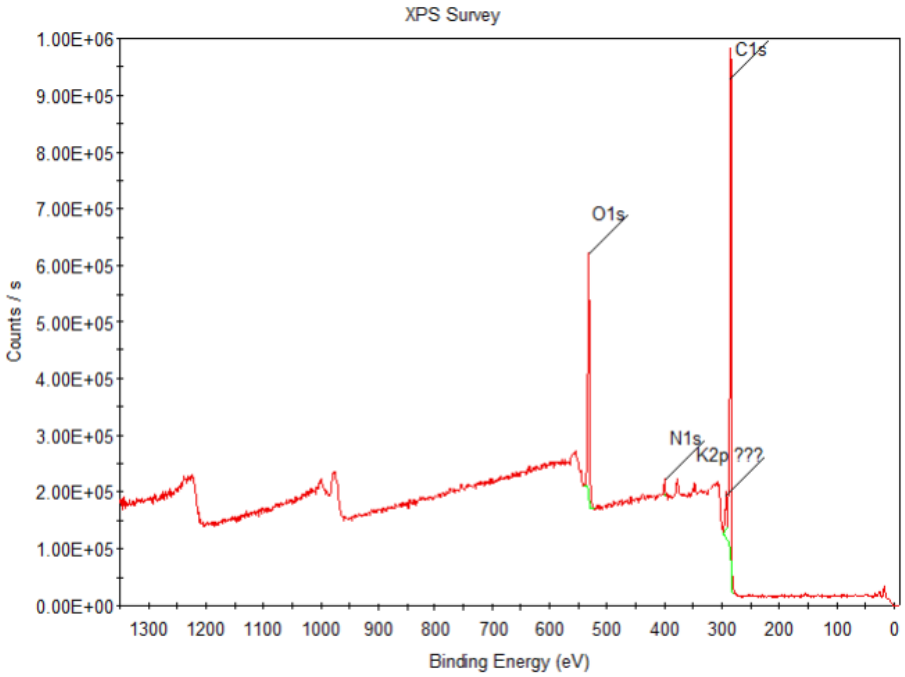
4.00E+05
3.00E+05
2.00E+05
1.00E+05
0.00E+00
Counts / s
C1s
O1s
N1s
1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0
Binding Energy (eV)

c.


XPS Survey
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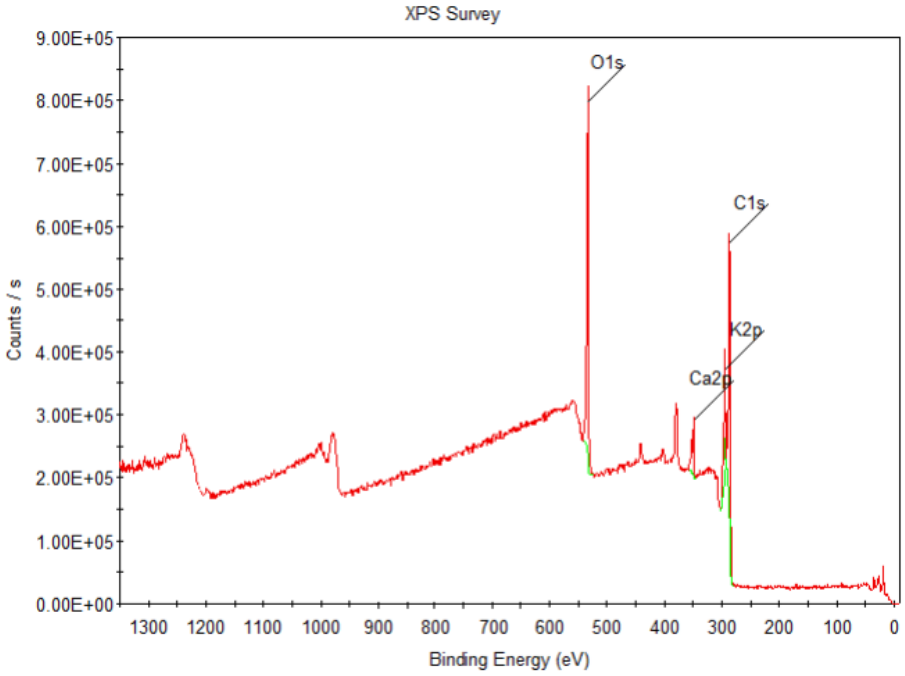
9.00E+05
8.00E+05
7.00E+05
6.00E+05
5.00E+05
4.00E+05
3.00E+05
2.00E+05
1.00E+05
0.00E+00
Counts / s
C1s
O1s
N1s
K2p
???
1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0
Binding Energy (eV)

d.


XPS Survey
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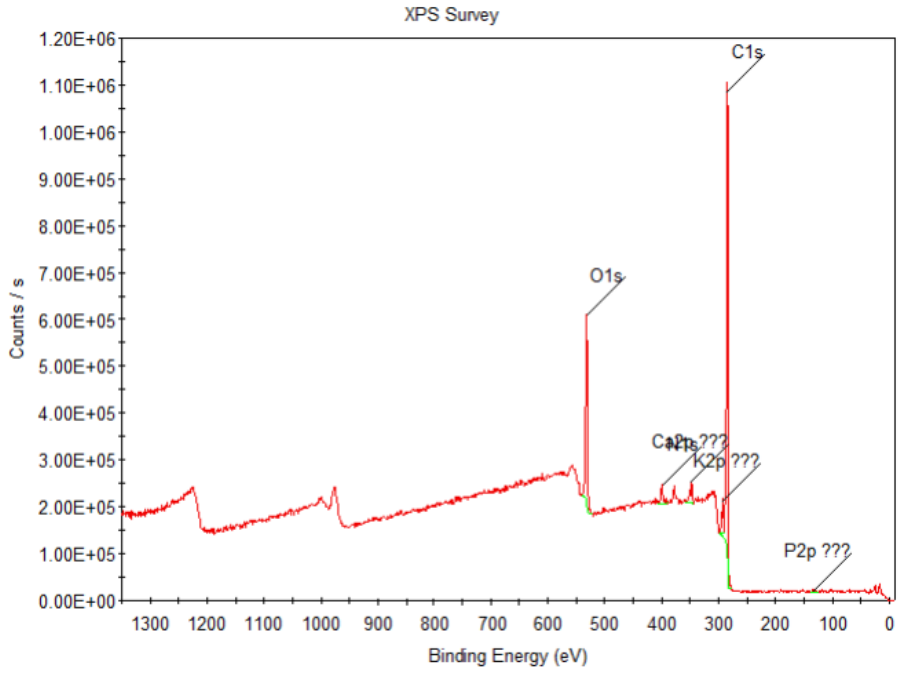
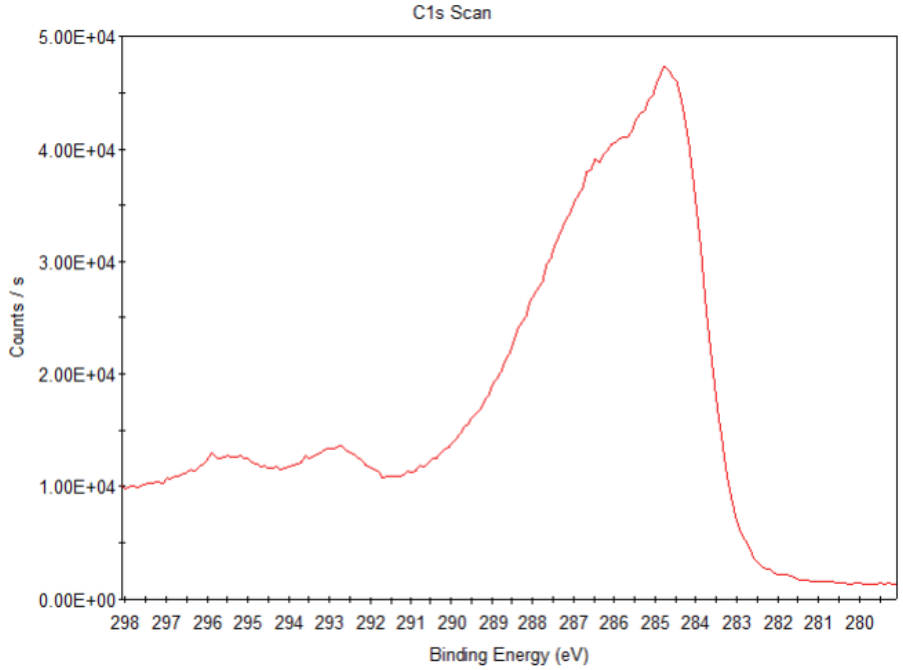
8.00E+05
7.00E+05
6.00E+05
5.00E+05
4.00E+05
3.00E+05
2.00E+05
1.00E+05
0.00E+00
Counts / s
O1s
C1s
K2p
Ca2p
1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0
Binding Energy (eV)

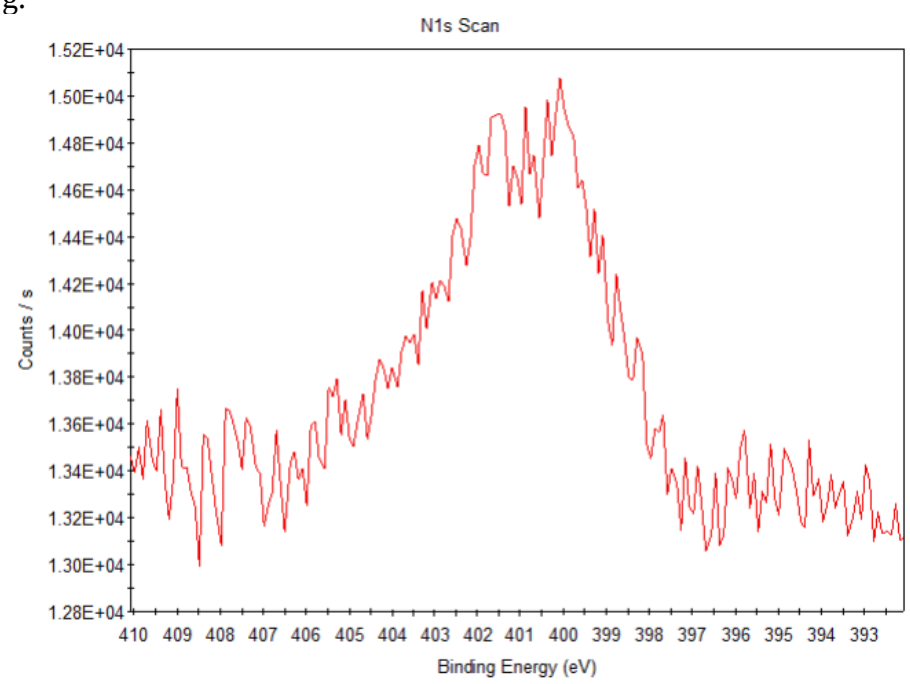
e.


XPS Survey
C1s
O1s
Ca2p ???
K2p ???
P2p ???
Counts / s
Binding Energy (eV)

f.


C1s Scan
Counts / s
Binding Energy (eV)

g.


N1s Scan
Counts / s
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1.38E+04
1.36E+04
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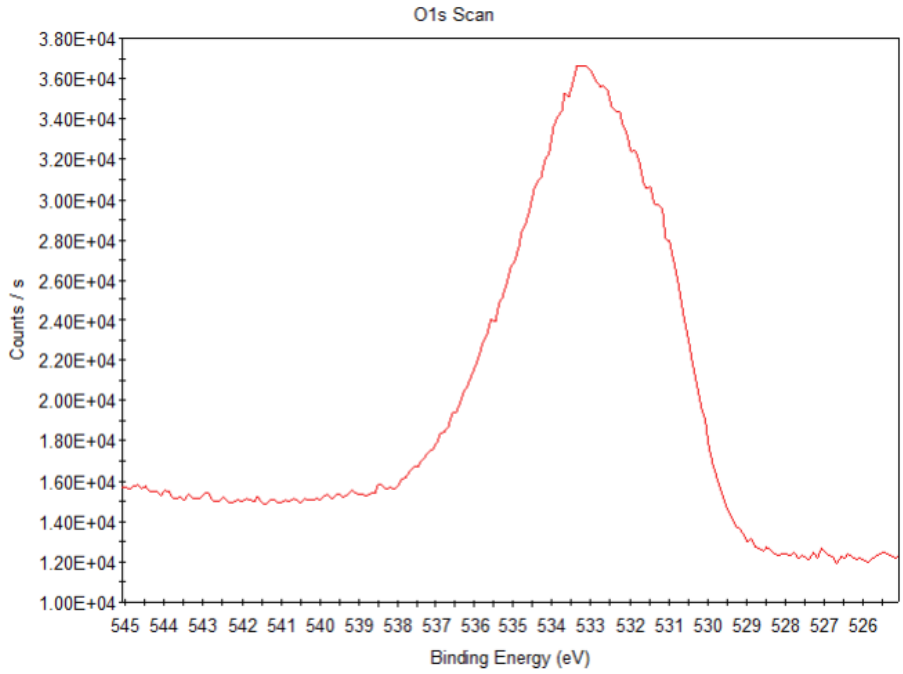
Binding Energy (eV)

h.


O1s Scan
Counts / s
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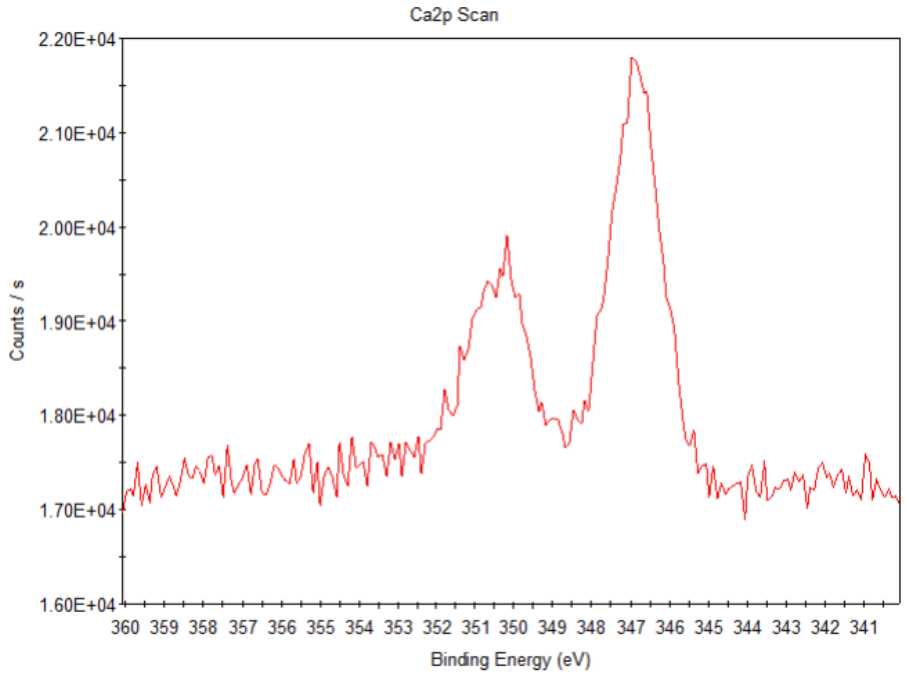
2.60E+04
2.40E+04
2.20E+04
2.00E+04
1.80E+04
1.60E+04
1.40E+04
1.20E+04
1.00E+04
545 544 543 542 541 540 539 538 537 536 535 534 533 532 531 530 529 528 527 526
Binding Energy (eV)

.

i.



j.

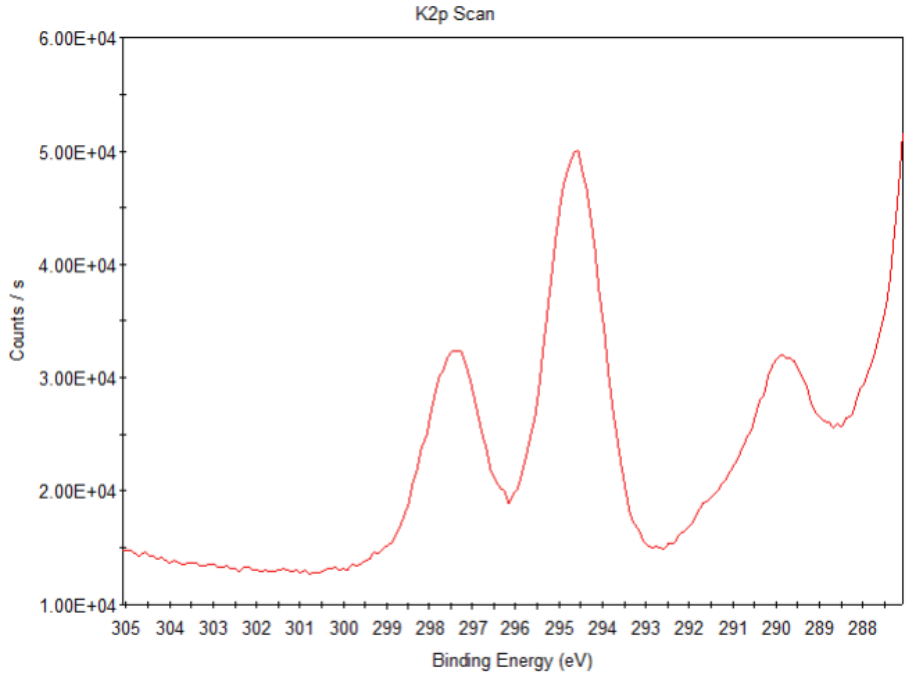


Figure S2 a-e) XPS survey scans indicating functional groups on the surface of the almond biochar. In total five scans were conducted, f-j) Scans for specific peaks seen in survey scans for the elements C, N, O, Ca, K, P.

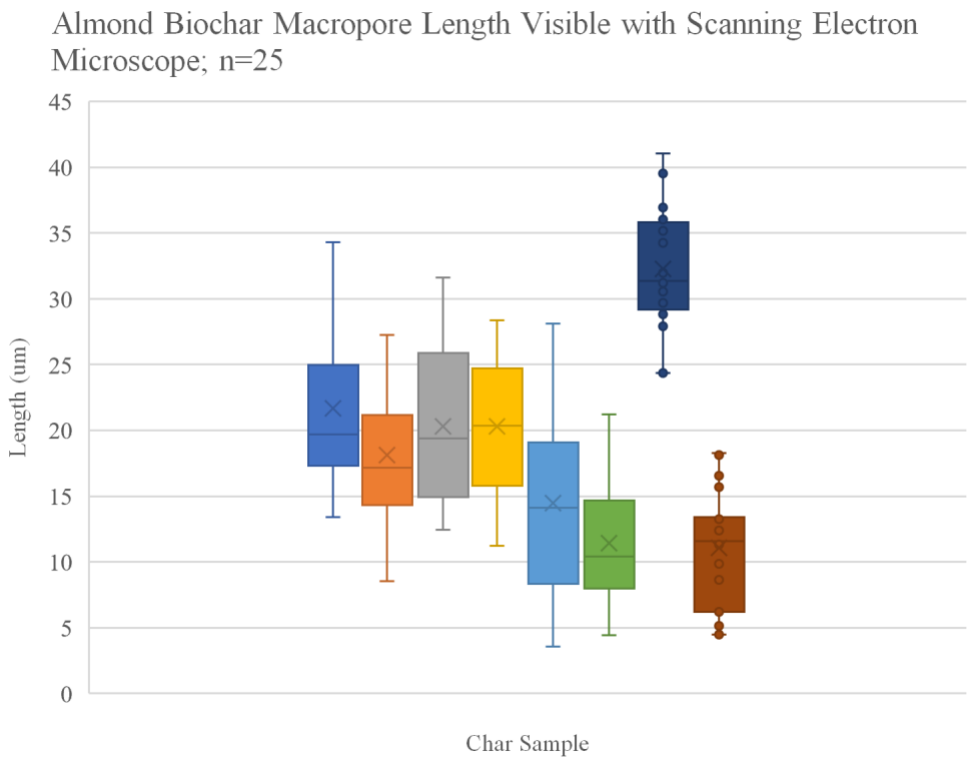


Figure S3 Almond Biochar Macropore Length Visible with Scanning Electron Microscope; n=25

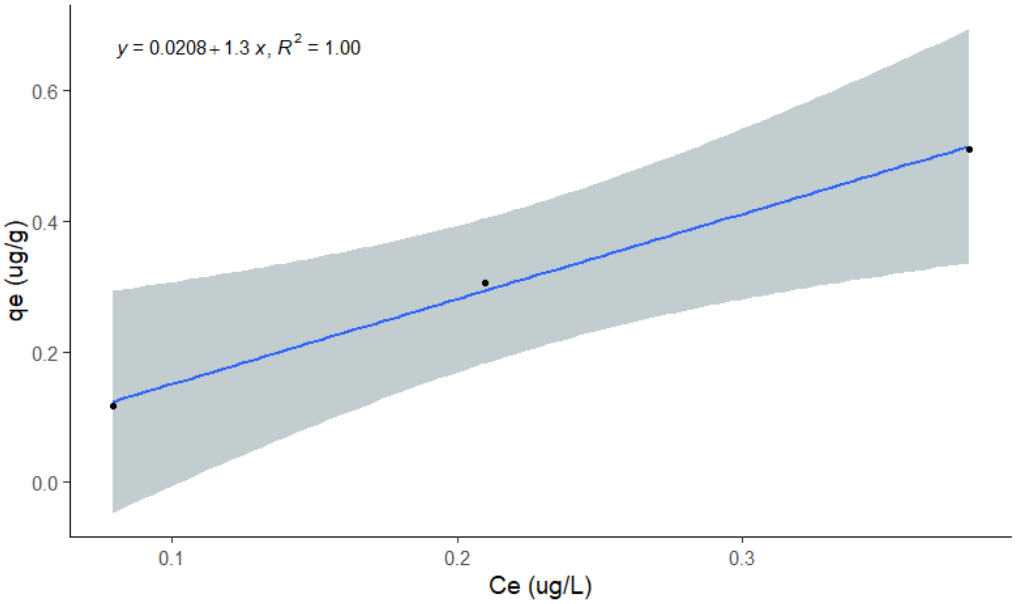


Figure S4 Linear isotherm of an HDPE plastic container and TCP solutions at equilibrium. error band represents a 95% confidence interval. Performed at 21.5°C.

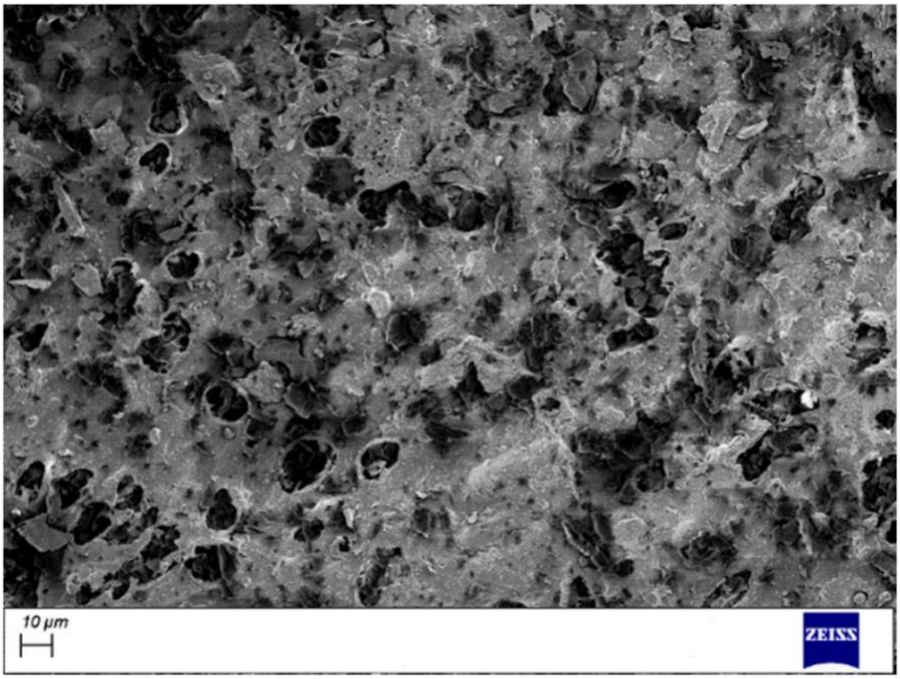


Figure S5: A 400 x magnification of the surface of the almond biochar used in this study. Macropores (darker ovals) were measured to estimate the mean length of pores (n=25) from seven different images.

Table S2 Preparing POU filters according to manufacturer's recommendations.

Filter type	Pre-conditioning instructions from the manufacturer
Pitcher 1	The pitcher, lid, and pour tray were washed with an unscented dish soap, and with mild soapy water and rinsed well. The filter was then rinsed for 15 seconds under running water. Finally, the first three pitchers of water were discarded.
Pitcher 2	The pitcher and dispenser, lid, and pour tray were washed with mild soapy water and rinsed well. The filter was then soaked in cold water for 15 minutes.
Pitcher 3	The pitcher and dispenser, lid, and pour tray were washed with mild soapy water and rinsed well.

Table S3 Flow rates in seconds for each filter type along different checkpoints of the manufacturer's estimated filter lifetime (MEL).

Filter type	% MEL	Filter 1 (mL/sec)	Filter 2 (mL/sec)	Filter 3 (mL/sec)	Mean flow rate (mL/sec)	Standard Deviation
Pitcher 1	0-25	4.54	4.99	4.30	4.61	0.35
	25-50	4.33	4.69	4.91	4.64	0.29
	50-75	4.20	4.69	4.45	4.45	0.24
	75-100	3.72	4.23	3.81	3.92	0.27
	100-125	3.50	4.18	3.84	3.84	0.34
Pitcher 2	0-25	5.45	6.99	4.64	5.70	1.19
	25-50	4.52	5.49	4.35	4.78	0.62
	50-75	5.50	5.16	5.69	5.45	0.27
	75-100	4.69	4.32	5.06	4.69	0.37
	100-125	4.53	4.53	4.79	4.62	0.15
Pitcher 3	0-25	2.56	1.36	3.12	2.35	0.90
	25-50	2.26	1.81	2.69	2.25	0.44
	50-75	3.12	2.69	2.67	2.83	0.26
	75-100	3.30	3.41	2.62	3.11	0.43
	100-125	0.29	3.06	0.33	1.23	1.59

Table S4 Percent reduction in TCP concentration along various (0, 25, 50, 75, 100, 125%) manufacturer's estimated lifetime checkpoints. $(C_{in} - C_{out})/C_{in}$

C_{out} at:	0% MEL	25% MEL	50% MEL	75% MEL	100% MEL	125% MEL
PPOU-1	97.0	98.9	98.9	96.6	96.1	96.0
PPOU-2	97.8	98.9	98.9	97.0	94.9	94.1
PPOU-3	96.6	98.9	98.9	93.1	87.7	No Data

Table S5 1,2,3-trichloropropane (TCP) removal in plastic containers at equilibrium.

Container	TCP at equilibrium (µg/L)	% TCP removal
Plastic bottle 1	0.079	19.4
Plastic bottle 2	0.21	19.2
Plastic bottle 3	0.18	18.2
Glass bottle 1	0.098	n/a
Glass bottle 2	0.26	n/a
Glass bottle 3	0.22	n/a