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The Fate and Risk of Oxyfluorfen Under Simulated California Rice Field Conditions

Author
Bonnar, David Joseph

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The Fate and Risk of Oxyfluorfen Under Simulated California Rice Field Conditions

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David Joseph Bonnar
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Approved:

Ronald S. Tjeerdema, Chair

Mathew J. Hengel

Kassim Al-Khatib

Committee in Charge

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ABSTRACT

Rice production in California is a thriving, multi-billion dollar industry, with the Sacramento Valley alone producing over 95% of the nation's short- and medium-grained rice. The sustainability of this industry is threatened, however, by the rapid evolution of herbicide resistant weeds spurred by long-term monoculture and a lack of herbicides with alternative modes of action. One agent proposed to ameliorate the lack of chemical control options is oxyfluorfen (OXY). OXY is a broad-spectrum, diphenyl ether herbicide that disrupts chlorophyll synthesis through inhibition of the protoporphyrinogen oxidase (protox) enzyme. It has demonstrated effectiveness against rice weeds, including weedy rice (*Oryza sativa f. spontanea*), a pest for which no herbicide is currently registered, and resistance to its mode of action has not been reported by rice growers. However, OXY is not currently registered for use with rice and its use in- or near-aquatic resources is currently prohibited due to its high toxicity to aquatic organisms. As rice field floodwater is ultimately released into nearby waterways, use of OXY with rice introduces the potential for its transport to the Sacramento River Basin where sensitive aquatic organisms may be harmed. Thus, it is imperative that registered uses be informed by a clear understanding of its transport and dissipation processes and potential for environmental impacts when it's used as a rice herbicide. To that end, it is the objective of this work to elucidate the environmental fate and aquatic risk of OXY when used as an herbicide in California rice fields.

Partitioning processes greatly influence overall fate by determining where a pesticide is found and which processes contribute most to dissipation. Thus, the soil-water partitioning behavior of OXY under simulated California rice conditions was characterized using a batch equilibrium method. Soil-water partitioning was investigated in two soils collected from

Sacramento Valley rice fields, at rice field temperatures (15, 25, 35 °C), and under various rice field salinity conditions. OXY showed high affinity for rice field soil (log[K_F] 2.92–3.44) that was largely concentration independent (N 0.87–1.08) and correlated with soil organic carbon (log[K_{oc}] 4.79–5.19) across all soil, temperature, and salinity treatments. Temperature enhanced binding affinity and bound OXY was poorly desorbed (9.3 to 27.0% desorption), exhibiting pronounced sorption hysteresis (HI > 0) in all treatments. These results indicate OXY is likely to concentrate in the sediment where it resists further dissipation, leading to persistence.

Volatilization from rice field water is recognized as a significant dissipation route for recalcitrant herbicides. Thus, the air-water partitioning behavior of OXY was investigated through determination of Henry's law constants (K_H) at rice field temperatures. A screening approach for evaluating the feasibility of experimental determination of K_H via gas-stripping method was developed and used to demonstrate that K_H cannot feasibly be measured for OXY; it must be calculated. Thus, K_H was calculated using four air-water partitioning models. Three (3) of the four models (EPI Suite, Kühne, and Two-Point Extrapolation) indicated that OXY is slightly volatile (K_H 3.00E-07−1.00E-05 atm·m^3·mol^{-1}) at rice field temperatures (15−40 °C), except at low temperatures (5−10 °C) where it is nonvolatile (K_H < 3.00E-07 atm·m^3·mol^{-1}). A single model (AQUAFAC-Sepassi) suggested OXY was substantially volatile (K_H > 1.00E-05 atm·m^3·mol^{-1}) at all rice field temperatures; however, investigation revealed limitations in the ability of the model to predict key physical properties for OXY, suggesting less robust results. Thus, the preponderance of evidence suggests OXY is nonvolatile to slightly volatile in California rice fields.

Partitioning and dissipation processes of OXY, in conjunction with anticipated use patterns in California rice fields, were then simulated using the Pesticides in Flooded

Applications Model (PFAM). Estimated environmental concentrations (EECs) were calculated under two (2) California rice field soil conditions and one standard soil condition, with water holding periods of 30 days and 0 days (no holding period). OXY concentrated heavily in sediment (21-day Avg Benthic Sediment EEC: 220,747−411,000 µg/kg-oc) with limited presence in water (21-day Avg Water Column EEC: 2.97−31.4 µg/L). Dissipation was slow and severely limited by microbial metabolism (anaerobic) in the sediment, with an effective half-life of 610.6 days for all treatments. While dissipation in the water column was substantially faster (Cumulative Effective Half-life: 9.4−10.5 days), its limited availability in water rendered OXY less sensitive to water column dissipation pathways. Consequently, water holding period had little effect on rice field and release water concentrations. Overall, these results indicate OXY is likely to accumulate in soil over time, leading to chronic exposure conditions for aquatic life as it slowly releases into water.

Risk to aquatic receptors was characterized using calculated EECs and in accordance with ecological risk assessment guidelines. Acute risk was generally low for water column animals (fish and invertebrates) and benthic invertebrates. However, chronic risk to freshwater fish (surrogates for aquatic-phase amphibians) under ultraviolet light conditions, chronic risk to benthic invertebrates, and risks to aquatic plants & algae exceeded risk thresholds under all conditions. California rice field soil conditions were associated with low acute risk ($RQ < 0.1$) and less risk overall compared to standard conditions. All risk conclusions were unaffected by holding time, suggesting that water management needs of growers should be considered when stipulating water holding periods for OXY. However, environmental monitoring is suggested to address accumulation and persistence concerns when OXY is applied to California rice field soil.

Chapter 1

Introduction

1.1 California Rice Agriculture

With over 500,000 acres planted statewide in 2023 and contributing more than $5 billion per year to our economy, rice is an important agricultural commodity in California.[1-2] Rice grown within the Sacramento Valley alone accounts for over 95% of California's total rice production and produces more short- and medium-grained rice than any other region within the United States.[3] The growing season generally begins between April and May with the aerial broadcast of pregerminated seed directly to the pre-flooded rice field, and extends until harvest, usually during the months of September and October. During this period, fields remain flooded at an approximate depth of 4 inches via continual exchange of water with the Sacramento River Basin in order to prevent algae growth, control weeds, and maintain favorable temperature conditions for rice growth.[4] Roughly 2 to 4 weeks from harvest, water is discharged from the field into the Basin to allow the field to dry out. After harvest, fields are reflooded and maintained through the winter (October to February) to facilitate straw decomposition and nutrient cycling. Rich with residual grain and native invertebrates, fields serve as important wildlife habitat for a variety of organisms during this period.[5] After winter flooding, fields are drained and prepared for the next growing season.

While floodwaters may be released at other times during the growing season, restrictions often apply. When fields are treated with pesticides, the potential exists for their discharge into receiving waters, risking exposure to wildlife, drinking water contamination, and transport to other agricultural fields.[5] Thus, pesticide labels usually mandate periods with which growers must hold water on their fields to allow pesticides to dissipate. These water holding periods are chemically specific and dependent on the overall dissipation rate of the pesticide, with typical durations spanning between 7 and 30 days.[4]

Under the warm and dry conditions of the Sacramento Valley, field water is sensitive to evapoconcentration of salts during holding periods.[6] This can have significant impacts on rice productivity as field salinities have been observed to reach 6.0 $dS \cdot m^{-1}$ early in the growing season, well surpassing the threshold for crop yield reduction of 0.88 $dS \cdot m^{-1}$.[6-7] Thus, growers are vested in ensuring field water is not held too long and must balance crop salinity requirements with effective weed management.

1.2 Herbicide Use and Resistance

In California, herbicides are the predominant type of pesticide used on rice both in acres treated and pounds applied.[3, 8] They are available in liquid or granular formulations and may be applied via foliar spray, as a pre-emergent to dry soil, or directly to flooded fields depending on the herbicide.[4] Among the most widely used are propanil, triclopyr (triethylamine salt), halosulfuron-methyl, and benzobicyclon.[8]

While a variety of herbicide products are registered for use, only seven modes of action are currently available for use with California rice.[9] Exacerbated by California's long-term monoculture rice production, the limited availability of herbicides with unique modes of action has driven the rapid evolution of herbicide resistance in weeds, including multiple-resistance, leading to substantial economic costs from yield loss.[9-12] Thus, growers seek to expand the selection of herbicides with alternative modes of action.

1.3 Oxyfluorfen

Oxyfluorfen [OXY; 2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl)benzene; Figure 1.1] is a broad-spectrum, diphenyl ether herbicide registered to control pre-emergent and post-emergent broadleaf and grassy weeds.[13] Commonly recognized by its trade name Goal®, OXY is widely used in both agricultural and nonagricultural settings, with most usage occurring within California.[14] Since it was first registered in 1979, OXY has emerged as one of the most widely applied herbicides in California and second only to glyphosate in the year 2021.[8]

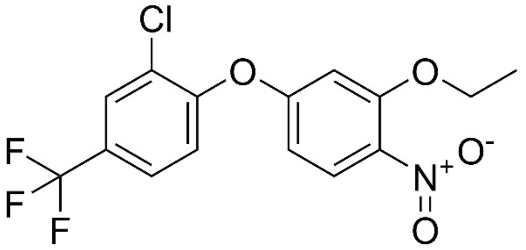

Figure 1.1. OXY, a diphenyl ether herbicide

OXY is an inhibitor of the protoporphyrinogen oxidase (protox) enzyme and acts through disruption of chlorophyll synthesis, leading to accumulation of phototoxic chlorophyll precursors.[13] The presence of light is also known to enhance its toxicity through generation of more activated oxygen species which attack and destroy cell membranes. Actively growing plants have increased susceptibility to these effects, rendering OXY particularly effective as a pre-emergent.[13]

OXY has demonstrated effectiveness against rice weeds, including weedy rice (*Oryza sativa f. spontanea*) which currently lacks any herbicides registered for its control.[9] Only one other herbicide registered in California, carfentrazone-ethyl (trade name Shark®), shares the same mode of action and weeds resistance problems for this active ingredient have yet to be reported. An OXY-tolerant rice strain has also been produced via non-transgenic methods and herbicide programs for use of OXY with tolerant rice are already in development.[9] Thus, OXY is widely anticipated by growers as a promising new herbicide that can be used to combat weed resistance and improve yields. However, OXY is not currently registered for use with rice and its use in- or near-aquatic resources is heavily restricted due to its high toxicity to aquatic organisms.[14]

Despite restrictions, OXY is frequently detected in aquatic resources. In samples collected across the U.S. between 1999 and 2018, the detection frequency of OXY was 1.3%, 4.1%, and 0.5% in surface water, sediment, and groundwater samples, respectively.[15] In California where OXY use is highest, it was detected in 41% of samples taken from agricultural waterways in Monterey, San Louis Obispo, Santa Barbara, and Imperial counties in 2016.[16] Detections have also been reported in urban waterways of Alameda, Contra Costa, Placer, Sacramento, and Santa Clara Valleys counties in 6% of samples taken in 2016.[17] Contamination of these non-target sites is thought to be the result of erosion transport via runoff as OXY binds tightly to soil particles and has limited water solubility.[18-19] Given the close connection between rice fields and the Sacramento River Basin, expanding the use of OXY to include rice further increases the potential for release into California waterways where it may impact sensitive species and environmental resources.

1.4 Environmental Fate

The environmental fate of a pesticide is a description of where the substance goes and how it transforms when released into the environment. It encompasses processes such as transport, degradation, and accumulation within various environmental media and organisms. These processes are driven by both the physiochemical properties of the chemical as well as its environment. In rice fields, the primary physiochemical properties influencing environmental fate are soil-water partitioning, air-water partitioning, photolysis, hydrolysis, and microbial metabolism (aerobic and anaerobic).[20] Current knowledge of these processes for OXY and their potential interactions with the unique properties of rice fields are discussed below.

1.4.1 Soil-Water Partitioning

The distribution of a chemical between soil and water phases is described by its soil-water partitioning behavior. Multiple phenomena contribute to this process, including adsorption, absorption, desorption, and hysteresis. The most frequent metrics used to characterize soil-water partitioning are the soil-water partition coefficient (K_d) and organic carbon-water partition coefficient (K_{oc}). These coefficients are calculated by dividing the concentration of compound sorbed (includes both adsorption and absorption) to soil or organic carbon fraction of soil for K_d and K_{oc}, respectively, by the concentration of compound within the aqueous phase (includes both free and dissolved organic carbon sorbed fractions). Commonly measured via batch equilibrium methods, these parameters are sensitive to experimental and environmental conditions, including temperature, salinity, soil properties, amount of compound in the system, and equilibration time.[21-24] For hydrophobic organic chemicals (HOCs), such as OXY, sorption isotherms are often constructed and fit to the Freundlich model to derive Freundlich isotherm parameters and characterize partitioning behavior.[21] Soil-water partitioning processes greatly influence overall dissipation rates as they direct the availability of pesticide within an environmental compartment, thereby determining which dissipation pathways are most relevant.

Reported sorption log(K_{oc}) and Freundlich coefficients (log[K_F]) for OXY range from 3.03 to 5.60 and from 1.23 to 2.36, respectively.[18, 25-29] These values suggest that OXY has a high affinity for soil organic matter, limiting its mobility through the soil profile and posing low risk of leaching to groundwater.[30-31] The reversibility of soil sorption has also been characterized by analyzing Freundlich isotherm parameters and found to be highly irreversible, indicating OXY is not readily released from the soil once it binds.[32] These behaviors suggest that OXY will concentrate in the sediment and resist release back into water; however, soil-water partitioning behavior has not been characterized for OXY in California rice field soils or under California rice field conditions (e.g., temperature, salinity, etc.).

1.4.2 Air-Water Partitioning

The air-water partitioning of a chemical is described by its Henry's law constant (K_H). K_H is a temperature dependent, equilibrium partitioning coefficient that is experimentally determined via the gas-stripping method.[33] However, this method often fails for HOCs possessing both low vapor pressure and poor water solubility, such as OXY.[34-36] In these cases, K_H may be estimated by dividing the vapor pressure of a chemical by its water solubility.[37] With a reported vapor pressure and water solubility of 4.66E-10 atm and 0.116 mg/L, respectively, at 25 °C, K_H has been calculated for OXY at 1.45E-06 $\text{atm}\cdot\text{m}^3\cdot\text{mol}^{-1}$. However, other sources have reported values as low as 2.35E-07 $\text{atm}\cdot\text{m}^3\cdot\text{mol}^{-1}$ at the same temperature and K_H values at other temperatures could not be located in the literature.[15] As K_H values below 3.00E-07 $\text{atm}\cdot\text{m}^3\cdot\text{mol}^{-1}$ indicate nonvolatility, and values between 3.00E-07 and 1.00E-05 $\text{atm}\cdot\text{m}^3\cdot\text{mol}^{-1}$ indicate slight volatility, estimates of K_H for OXY straddle between two major volatility categories. This suggests that the air-water partitioning behavior of OXY may be particularly sensitive to the seasonal temperature variations observed in rice fields, where temperatures can fluctuate between 5 to 38 °C.[38-39]

1.4.3 Photolysis

Sunlight-induced photodegradation may occur when a chemical either absorbs a photon (direct photolysis) or reacts with another species that has been activated by a photon (indirect photolysis). Overall, the photolytic behavior of OXY is well-studied. Absorption spectra for OXY range from 267–276 nm and 310–325 nm; however, direct photolysis of OXY in the environment depends primarily on absorption above 290 nm, which is the solar cutoff.[37, 40] OXY readily undergoes aqueous photolysis, with reported half-lives ranging from 4.3 hours to 7.5 days depending on lighting conditions.[29, 41-44] OXY is also reported to undergo photolysis on soil surfaces, with reported first order half-lives ranging from 36 minutes to 28 days, and second order half-lives ranging from 0.16 to 0.246 $kg \cdot mg^{-1} \cdot h^{-1}$ depending on soil and lighting conditions.[29, 43-46]

In rice fields, photodegradation of OXY is likely to be rapid in clear, shallow waters under intense California sunlight.[13] However, California rice floodwaters are frequently rich in dissolved organic carbon (DOC) which can mediate the enhancement or quenching of photolysis while also limiting sunlight penetration by contributing to turbidity.[47-49] In soil, photolysis depth is limited to less than 1.0 mm for both direct and indirect mechanisms.[50] On soil surfaces, enhancement or quenching of photolysis may also be mediated by humic substances.[51] Lastly, rice crop progressively attenuates the availability sunlight as it grows, providing shade to the field.[20]

Although the photolysis of OXY has been evaluated extensively under a variety of conditions, it has not been characterized under California rice field conditions. Given the dynamic range of modulating factors at play, effective photolysis rates in rice fields may be substantially different than those observed under controlled experimental conditions.

1.4.4 Hydrolysis

OXY does not degrade via hydrolysis at environmentally relevant pH levels and temperatures.[15]

1.4.5 Microbial Metabolism

Metabolism of pesticides by microbes (biodegradation) may occur in the environment under aerobic and anaerobic conditions. Aerobic conditions include biodegradation in the soil or water column in the presence of oxygen, while anaerobic conditions are observed in anoxic sediment conditions. The rate of microbial metabolism varies with microbial community and is sensitive to environmental conditions such as temperature, salinity, and reduction-oxidation (redox) potential.[52-55] Organic carbon content is also thought to play a significant role in overall biodegradation rates of HOCs as pesticides are less bioavailable in their sorbed state.[24, 56]

Biodegradation of OXY in soil varies widely and is strongly dependent on soil conditions, particularly the level of organic matter, with reported half-lives ranging from 15 to 296 days.[25, 28, 46, 57-60] Similarly, the rate of water column aerobic metabolism varies widely for OXY, with reported half-lives ranging from 4 to 660 days.[15, 56, 61] In anaerobic sediment, the half-life of OXY is reported to range from 3 to 603 days, with degradation occurring rapidly under sandy and low organic carbon soil conditions.[46, 56-57, 61-62]

In rice fields, aerobic soil conditions are observed prior to flooding. After flooding, anaerobic conditions are quickly established throughout the field, although oxic regions may persist within a few millimeters of the water column surface.[63] While microbial metabolism is well studied for OXY, its biodegradation in California rice fields has not been characterized. Given that rice fields vary in features influencing microbial metabolism (e.g., temperature, salinity, soil conditions, etc.), it is important that proper consideration be given to these modulating factors in experimental or modeling designs.

1.5 <u>Research Goals and Objectives</u>

This research characterizes the fate and aquatic risk of OXY under simulated California rice field conditions. Focus is given to partitioning processes, which greatly influence overall fate, and the influence of temperature, salinity, and soil conditions. Environmental concentrations of OXY and its dissipation behavior are predicted using a validated rice field fate model. Exposure and risk to aquatic organisms are characterized in accordance with standard ecological risk assessment guidelines. Lastly, the effects of water holding time on risk outcomes was evaluated to determine effective water holding period durations. The research will aid regulatory agencies and California rice growers develop and implement safe and effective use practices for OXY in California rice fields.

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Chapter 2

Soil-Water Partitioning Behavior of Oxyfluorfen Under California Rice Field Conditions

Published David J. Bonnar, Jeff P. Eichler, Sanjai J. Parikh, Andrew Blandino, Rebecca A. Lybrand, Madison L. Morris, Matt J. Hengel, and Ronald S. Tjeerdema

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2.1 Abstract

The herbicide oxyfluorfen [OXY; 2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl)benzene] has recently surged in interest among rice farmers with the development of OXY-tolerant rice and its demonstrated effectiveness against problematic rice-weeds in California. Not currently registered for use with rice, its fate in rice fields is poorly understood. Using a batch equilibrium method, we characterize the soil-water partitioning behavior of OXY under simulated California rice field conditions. Sorption data imply strong, primarily concentration independent binding correlated with soil organic carbon (Log[K_{oc}] 4.79 – 5.19; N 0.87 – 1.08) across all soil, temperature, and salinity treatments. Temperature significantly enhanced binding affinity for sorption and desorption processes ($P < 0.01$). Bound OXY was poorly desorbed (9.3% to 27.0% desorption) from rice soils and exhibited significant sorption hysteresis ($HI > 0$) in all treatments. These results indicate that OXY will predominantly remain in soil, resistant to release into water in California rice fields.

2.2 Introduction

Oxyfluorfen (OXY, trade name Goal) is a broad-spectrum, diphenyl-ether herbicide used for pre- and post-emergent control of broadleaf and grassy weeds.[1] First registered in 1979, OXY has seen wide use in both agricultural and non-agricultural settings, with the majority of agricultural usage occurring within California.[2]

Despite entering the market over 40 years ago, interest in its use in California rice fields has piqued recently due in part to technological advancements such as the development of non-transgenic, OXY-tolerant rice strains and research indicating effective control of rice weeds.[3-4] Of particular interest to growers, OXY has been shown to be effective against the rice weed *Oryza sativa f. spontanea* (weedy rice), a pest for which no herbicides are currently registered for in California.[4] Although there are currently no OXY products registered for use in rice fields, efforts are underway to bring them to market.[3-4] Use in rice fields represents a new use pattern for OXY as all currently registered products in the U.S. contain general and explicit prohibitions against applications in- or near-aquatic resources, due in part to its high toxicity to aquatic organisms.[1-2] Despite the use restrictions, OXY has been frequently detected in sediment and surface water and use within rice fields enhances the potential for release into adjacent waters.[5-6] Thus, the fate of OXY under California rice field conditions must be well understood to inform effective and environmentally protective use practices.

Most rice produced in California is grown within the Sacramento Valley, where growers flood fields before planting and maintain water levels at approximately 10 cm throughout the growing season.[4, 7] These waters often experience seasonal temperature variations, with observed fluctuations ranging from 5 to 38 °C.[8-9] At higher temperatures, evapoconcentration can increase field salinity, with levels reaching up to 6.0 $dS \cdot m^{-1}$ in some California fields.[10] As 0.88 $dS \cdot m^{-1}$ is the salinity threshold for crop yield reduction, growers are vested in ensuring field water is not held for too long.[10-11] However, when herbicides are applied, water holding periods are regularly imposed, limiting how early water can be released from fields to allow herbicides to dissipate.[12]

The period for an herbicide to dissipate below levels of concern is chemically specific and depends on its properties and fate.

One of the most influential processes governing herbicide fate is soil-water partitioning.[13] Frequently characterized by the partition coefficient, K_d, it is the primary chemodynamic process responsible for how much herbicide is found in soil versus water. Measurement of K_d is impacted by temperature and salinity levels, which influence aqueous solubility and sorption to sediment.[14-15] Soils rich in organic matter and clay content, such as rice fields, are known to strongly bind non-polar, hydrophobic chemicals such as OXY, and bound herbicides may not be readily desorbed.[16-17]

Although rice fields are unique agricultural environments that vary considerably in environmental conditions pertinent to chemical fate, the soil-water partitioning of OXY has not been characterized in California rice fields. Thus, this study's overarching objective is to investigate the soil-water partitioning behavior of OXY under simulated California rice field conditions. Specifically, 1) the batch equilibrium method is used to evaluate OXY sorption and determine K_d and the organic carbon-water partitioning coefficient (K_{oc}) in two California rice field soils under simulated California conditions (e.g., temperature, salinity); 2) the organic matter characteristics and mineralogy of the soils are profiled; and 3) desorption processes are characterized to evaluate sorption reversibility.

2.3 Materials and Methods

2.3.1 Chemicals

2-Chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl)benzene (OXY; 98%) was purchased from Ontario Chemicals, Inc. (Guelph, ON). Water (Optima grade), methanol (Optima grade), acetonitrile (HPLC grade), sodium chloride (99%), and calcium chloride (100%) were purchased from Fisher Scientific (Fair Lawn, NJ). Formic acid (98%) was purchased from Honeywell International, Inc. (Muskegon, MI). Water (HPLC grade), ethyl acetate (HPLC grade), 2-chloro-1-(3-ethoxy-d6-4-nitrophenoxy)-4-(trifluoromethyl)benzene (d5-OXY; 98%), magnesium sulfate, and sodium sulfate were purchased from Sigma-Aldrich (St. Louis, MO).

2.3.2 Soil Preparation and Analysis

Soils were collected from two separate rice fields near Davis, CA (38.543936, -121.650750; Riz-Sycamore clay loam), and in Biggs, CA (39.451826, -121.719226; Esquon-Neerdobe fine, smectic, flood basin soil).[18-19] They were collected from the top 10 cm of each field, air-dried, and sieved (<2 mm) for use in partitioning experiments. Soil properties, including texture, fractions organic matter (f_{om}), fraction organic carbon (f_{oc}), and cation exchange capacity (CEC) were characterized by the UC Davis Analytical Laboratory while soil pH was measured according to methods described by US Salinity Laboratory Staff.[20-21] A summary of these properties is presented in Table 2.1.

Table 2.1 Rice Field Soil Properties[a]

soil	texture[b]	sand (%)	silt (%)	*clay (%)*	f_{om}	f_{oc}	pH	CEC (meq/100g)
Davis	clay loam	22	43	35	0.0415	0.0241	6.42	37.3
Biggs	clay loam	33	40	27	0.0277	0.0161	5.37	20.2

[a]Abbreviations: fraction organic matter (f_{om}), fraction organic carbon (f_{oc}), cation exchange capacity (CEC)
[b]Texture defined according to Natural Resources Conservation Service soil texture classification.

Soil organic matter (SOM) content and soil mineralogy were qualitatively analyzed using Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD), respectively. Methodologies for these analyses are presented in the Supporting Information.

2.3.3 Soil-Water Partitioning

Sorption and desorption isotherms were constructed according to OECD 106 batch equilibrium method guidelines.[22] The optimal soil-to-solution ratio of 1:600 (0.25 g of soil and 150 g of 0.01 M $CaCl_2$ water) was determined during preliminary studies and selected for all isotherms. Additional preliminary studies also showed sorption and desorption pseudo-equilibration durations of 48 and 24 h, respectively, and that OXY was stable to degradation (e.g., hydrolysis and biotic) throughout the experiment. Soil-water samples were prepared in 150 mL crimp-top glass serum bottles and equilibrated overnight in a MaxQ 6000 temperature-controlled shaker (265 rpm) (Thermo Scientific, Waltham, MA). Samples were then spiked to initial concentrations of 0.009, 0.015, 0.03, 0.05, or 0.09 $\mu g \cdot g^{-1}$ OXY in the aqueous phase (acetonitrile concentration did not exceed 0.1%). Three replicates for each spike level and a negative control were prepared for each experiment. Spiked samples were shaken (265 rpm) for 48 hours prior to centrifugation (1573 *g*, 15 min) and liquid-liquid extraction of aqueous phase aliquots (described below). The remaining aqueous phase was then decanted and replaced with 150 g of fresh 0.01 M $CaCl_2$ aqueous solution to prepare samples for desorption analysis. Desorption samples were shaken (265 rpm) for 24 hours before centrifugation (1573 *g*, 15 min) and liquid-liquid extraction of the aqueous phase under the same conditions as the sorption analysis. The experiment was repeated for both soils at equilibration temperatures of 15, 25, and 35 °C (± 1 °C). An additional set of isotherms at 25 °C (± 1 °C) were prepared under the same conditions as before, except with an aqueous phase mixture of either 0.01 M and 0.05 M NaCl, $CaCl_2$, $MgSO_4$, and Na_2SO_4 at a 10:1:2:1 molar ratio. These salinity levels (approx. 1.2 and 6.0 $dS \cdot m^{-1}$) and salt composition were selected to simulate observed California rice field salinity (RFS) conditions.[10-11]

2.3.4 Aqueous Phase Extraction

Five (5) mL of aqueous phase was transferred to 15 mL polypropylene centrifuge tubes followed by 5 mL of ethyl acetate. Tubes were capped and shaken vigorously by hand for 2 minutes. The samples were allowed to settle before transferring 3.5 mL of the organic layer to borosilicate test vials and evaporating to dryness under gentle N_2 flow in a water bath (50 °C). Samples were reconstituted with 3.5 mL acetonitrile containing 0.01 $\mu g \cdot mL^{-1}$ d5-OXY internal standard, vortexed, then filtered (0.2 µm, PTFE) into sample vials for liquid chromatography-tandem mass spectrometry analysis. Preliminary investigations indicated no loss of OXY due to filtration. Spike recovery was evaluated in control bottles containing a spiked aqueous phase. Average spike recovery (±SE) at a fortification level of 0.015 $\mu g \cdot g^{-1}$ was 95% ± 1.8% ($n = 3$). Sorption of analyte to container walls was determined to be a source of loss in these control samples, with extractable residues typically less than 0.5% and not exceeding 1.12% of the applied amount. Correction for container sorption, however, was deemed unnecessary as the presence of soil is known to mitigate this loss and no extractable residues were detected on container walls in preliminary studies of samples containing soil.[22]

2.3.5 LC-MS/MS Analysis

Sample extracts were analyzed with an Agilent 1260 Infinity series high-pressure liquid chromatograph (HPLC) (Santa Clara, CA) in tandem with an Agilent 6420 triple quadrupole mass spectrometer (QQQ) using electrospray ionization in positive mode. Sample injections (10 µL) were made onto an Agilent ZORBAX Eclipse XDB-C18 column (4.6 mm × 150 mm; 5 µm) and eluted with isocratic mobile phase composed of 90% methanol (0.1% formic acid) and 10% water (0.1% formic acid) at 0.5 $mL \cdot min^{-1}$. A deuterated isotope of oxyfluorfen, d5-OXY, was included as an internal standard to account for instrumental variation as matrix effects were not observed in preliminary studies. Retention times for both OXY and d5-OXY were 5.6 min with a stop-time of 8 minutes. Mass analysis was performed using multiple transition monitoring. Selected quantitative and qualitative ions for OXY were 362 → 316 $m \cdot z^{-1}$ and 362 → 237 $m \cdot z^{-1}$, and 367 → 237 $m \cdot z^{-1}$ for d5-OXY. Linear calibration curves were constructed over five concentrations between 0.0005—0.5 $\mu g \cdot mL^{-1}$ oxyfluorfen in acetonitrile (R^2 0.996—0.999). Additional mass spectrometer acquisition parameters are available in Supporting Information (Table S2.1).

Method detection limits (MDL) and method quantitation limits (MQL) were determined by analyzing blank extracts ($n = 7$) spiked to 0.001 $\mu g \cdot mL^{-1}$ OXY in acetonitrile. The MDL and MQL were calculated by multiplying the standard deviation of the replicate spiked blanks by 3.1427 (single-tailed 99th percentile t-statistic) and 10, respectively. For Davis soil treatments, the MDL and MQL were 0.00031 and 0.00099 $\mu g \cdot mL^{-1}$, respectively. For Biggs soil treatments, the MDL and MQL were 0.00006 and 0.00019 $\mu g \cdot mL^{-1}$, respectively.

2.3.6 Partitioning Coefficients

The concentration of OXY in the aqueous phase after equilibration was determined directly from aqueous phase extracts. Consistent with method standards outlined by OECD 106 guidelines, concentration in soil at equilibrium was calculated via the measure by difference method.[13, 22] For all calculations, soil mass refers to oven dry mass which is the weight of soil corrected for moisture content.

The concentration in the soil at sorption equilibrium was calculated according to equation (2.1):

$$q_s^s = \frac{m_{aq} \cdot \left(C_i - C_{aq}^s\right)}{m_s} \tag{2.1}$$

where m_{aq} and m_s are the mass (g) of the aqueous phase and soil, respectively, C_i is the initial aqueous concentration of OXY (µg·g^{-1}), and q_s^s and C_{aq}^s are the concentration of OXY (µg·g^{-1}) in soil and aqueous phase at sorption equilibrium, respectively.

The concentration in the soil at desorption equilibrium was calculated according to equation (2.2):

$$q_s^d = \frac{C_i \cdot m_{aq}^i - (C_{aq}^s \cdot m_{aq}^{dec} + C_{aq}^d \cdot m_{aq}^r)}{m_s} \tag{2.2}$$

where m_{aq}^i is the initial aqueous phase mass (g), m_{aq}^{dec} is the mass of aqueous phase decanted (g), m_{aq}^r is the mass of aqueous phase after replacing the mass of the decanted liquid (g), and q_s^d and C_{aq}^d are the concentration of OXY (µg·g^{-1}) in soil and aqueous phase at desorption equilibrium, respectively.

The soil-water partition coefficient (K_d) and organic carbon-water partition coefficient (K_{oc}) were calculated from data obtained from the second lowest initial concentration ($C_i = 0.015$ µg·g^{-1}) according to equations (2.3) and (2.4):

$$K_d = \frac{q_s^s}{C_{aq}^s} \tag{2.3}$$

$$K_{oc} = \frac{K_d}{f_{oc}} \tag{2.4}$$

where f_{oc} is the fraction of organic carbon of the soil (Table 2.1).

2.3.7 Freundlich Isotherms

Sorption and desorption isotherms were constructed by plotting the equilibrium concentration in soil, q_s, versus the equilibrium concentration in water, C_{aq}, for the various treatment groups. Isotherms were then fit to the log transformed Freundlich equation (2.5):

$$\log(q_s) = N \cdot \log(C_{aq}) + \log(K_F) \tag{2.5}$$

where q_s and C_{aq} are the equilibrium concentration OXY sorbed to the soil and water ($\mu g \cdot g^{-1}$), respectively, N is the Freundlich exponent, and K_F is the Freundlich constant.

2.3.8 Hysteresis

The degree of sorption-desorption hysteresis was quantified through calculation of the hysteresis index (*HI*) according to equation (2.6):

$$HI = \frac{q_e^d - q_e^s}{q_e^s} \tag{2.6}$$

where q_e^d and q_e^s are the solid-phase solute concentrations for a single-cycle sorption and desorption experiment, respectively, and are calculated at a particular residual solution phase concentration (C_e) using the Freundlich parameters.[23] A zero or negative *HI* value indicates that hysteresis is insignificant, while values greater than 0 indicate increasing degrees of sorption-desorption hysteresis.[24] Lower and upper bound C_e for calculation of *HI* were selected based on the observed sorption and desorption isotherm ranges for each treatment.

2.3.9 Statistics

The effect of soil, temperature, and saline environment on Freundlich parameters of equation (2.5) was assessed using a weighted linear regression model with separate N and $\text{Log}(K_F)$, the slope and intercept, respectively, for each experimental treatment combination of soil, temperature, and saline environment for both sorption and desorption processes. The same model was used to calculate *HI* of equation (2.6) as a transformation of equation (2.5) for both sorption and desorption isotherms and for each treatment combination.

Due to the presence of measurement error for both C_{aq} and q_s at each C_i, which can bias model estimates of Freundlich parameters, the regression model was fit on the average of three replicate values for q_s and C_{aq} at each C_i and for each treatment combination in order to reduce such bias. Exploratory analysis demonstrated heteroskedasticity of model residuals across different treatments with standard linear regression and, as a result, weighted linear regression was considered instead.

Data were analyzed using R statistical software (Vienna, Austria) using the **nlme** R package with the gls() function for weighted least squares.[25-26] A significance level (α) of 0.05 was selected and results where $P \leq 0.05$ were considered statistically significant.

2.4 Results and Discussion

2.4.1 Soil Organic Matter and Mineralogy

Figure S2.1 in the Supporting Information provides FTIR spectra to compare the mineral and SOM compositions of the Davis and Biggs soils. Few differences can be observed in the spectra of the unaltered soil samples (spectra c and d) which include both mineral and SOM fractions; however, examining the SOM spectra (spectra a and b) reveals notable differences between the two soils.

Both samples show IR peaks consistent with those attributed to aromatic carbon (1552 cm^{-1}) and carboxylic acids (1548 and 1425 cm^{-1}). The primary difference between the SOM spectra is that the organic peak intensities are greater for the Davis soil than the Biggs soil, which is consistent with the f_{oc} values reported in Table 2.1. The peak at 1710 cm^{-1} in spectrum b represents carbonyl (C=O) due to the protonation of carboxyl groups—which is explained by the lower pH of the Biggs soil (Table 2.1). The general carbon chemistry appears similar for the two soils, which is further demonstrated via examination of the relative ratio of the aromatic peak (1552 cm^{-1}) to the carboxyl peaks (1548 and 1425 cm^{-1}) of the OM spectra: Davis 1552:1548 = 1.14, Davis 1552:1425 = 1.18, Biggs 1552:1548 = 1.18, Biggs 1552:1425 = 1.13.

Figure S2.2 in the Supporting Information provides X-ray diffractogram patterns for mineralogical characterization. The primary mineral composition for the Biggs and Davis surface soils were relatively similar in that both samples were dominated by quartz and plagioclase feldspar minerals, with more minor amounts of mica and secondary clays (Figure S2.2). The primary mineral assemblage for the Biggs soil was dominated by quartz and feldspars (i.e., labradorite and albite; Figure S2.2a), which was comparable to the Davis soil that was also predominately quartz and feldspar minerals (i.e., albite and oligoclase; Figure S2.2b). The 9.95 Å peak indicative of mica (i.e., phlogopite) was most pronounced in the Davis sample versus a much lower intensity peak expression in the Biggs sample. Peaks observed in the lower d-spacing range of the bulk Davis sample also suggested the presence of vermiculite (14.1 Å), illite (10.1 Å), and kaolinite (7.2 Å). The clay diffractogram pattern for the Biggs soil confirmed the presence of kaolinite, vermiculite, illite, as well as an interlayered mineral that was distinguished by partial collapse following the KCl-550 heat treatment (Figure S2.2c). There was also little to no smectite present in the Biggs soil compared to a well-expressed peak at 18.4 Å indicative of smectite at in the Davis soil following Mg+Glycerol treatment. The clay mineral assemblage of the Davis soil was composed of smectite, vermiculite, kaolinite, illite, and an interlayered mineral species as indicated by the partial collapse to 10.1 Å following the KCl-550 heat treatment (Figure S2.2d).

2.4.2 Soil Sorption

Sorption Freundlich parameters and log(K_{oc}) by treatment are summarized in Table 2.2, while Freundlich isotherms (untransformed and log transformed) are available in the Supporting Information (Figure S2.3 and Figure S2.4). The percentage of OXY sorbed ranged from 62.2% to 84.6% with an average (±SE) of 71.3 ± 0.8%, which is within the ideal range (>50%) for characterizing sorption.[22] Sorption log(K_{oc}) ranged from 4.79 to 5.19, indicating high affinity of oxyfluorfen for the soil and in general agreement with values reported previously in the literature (3.03 – 5.60).[16, 27-30] With this affinity, OXY is classified as hardly mobile to immobile in soil and as a non-leacher posing minimal risk of leaching to groundwater from rice field soils.[31-32] Biggs soil treatments yielded greater log(K_{oc}) than Davis soil, except for 0.05 M RFS treatments. For $CaCl_2$ treatments, log(K_{oc}) also increased significantly with temperature for both soils (P = 0.00807). This pattern is consistent with previous observations that sorption to rice field soil is enhanced with temperature and is indicative that the effects of temperature had a greater impact on the affinity of OXY for the soil than increases in its solubility.[33-34] It is possible that temperature increases may lead to release of water layers attached to soil surfaces, facilitating the liberation of adsorption sites previously occupied by water molecules.[35] Increased diffusion into the SOM matrix and changes in SOM structure at higher temperatures may have also played a role.[36-37] No significant differences in log(K_{oc}) were found between RFS and $CaCl_2$ treatments or with increased rice field salinity.

Sorption isotherms were well described by the transformed Freundlich model (R^2 0.971 − 0.998), with OXY displaying ideal C-curve isotherm behavior characteristic of hydrophobic organic chemicals (HOCs) for most treatments.[13] S-curve isotherms for OXY in soil have also been described in the literature.[29, 38-39] The patterns observed in these studies may lack environmental relevance, however, due to limitations in design, including the use of only three initial concentrations and exceedance of the aqueous solubility of OXY (0.1 μg·mL^{-1}, 25 °C) for all initial concentrations.|

Table 2.2 Freundlich Parameters for Sorption of OXY in California Rice Field Soils[a,b]

soil	temperature (°C)	salinity (M)	log(K_{oc})[c] ± SE	N ± SE	log(K_F) ± SE	R^2
Davis	15	0.01 $CaCl_2$	4.79 ± 0.02 a	1.08 ± 0.10 ab	3.36 ± 0.22 a	0.984
	25	0.01 $CaCl_2$	4.82 ± 0.04 ab	0.92 ± 0.02[d] ab	3.02 ± 0.05 a	0.998
	35	0.01 $CaCl_2$	5.00 ± 0.01 ab	1.00 ± 0.11 ab	3.44 ± .026 a	0.978
	25	0.01 RFS	4.82 ± 0.04 ab	0.99 ± 0.08 ab	3.19 ± 0.16 a	0.973
	25	0.05 RFS	4.87 ± 0.04 ab	0.88 ± 0.09 ab	2.92 ± 0.18 a	0.988
Biggs	15	0.01 $CaCl_2$	4.88 ± 0.03 b	1.01 ± 0.14 ab	3.13 ± 0.29 a	0.971
	25	0.01 $CaCl_2$	5.07 ± 0.01 ab	0.99 ± 0.08 ab	3.17 ± 0.16 a	0.977
	35	0.01 $CaCl_2$	5.19 ± 0.07 ab	0.87 ± 0.02[d] b	3.05 ± 0.04 a	0.998
	25	0.01 RFS	4.86 ± 0.06 ab	1.05 ± 0.04 a	3.20 ± 0.09 a	0.994
	25	0.05 RFS	4.83 ± 0.02 ab	1.01 ± 0.02 a	3.08 ± 0.05 a	0.998

[a] Letters indicate statistically significant differences between treatments. Values with the same letter are not significantly different, while those with different letters are statistically distinct ($\alpha = 0.05$).

[b] Abbreviations: oxyfluorfen (OXY), rice field salinity (RFS) with molar ratio of 10:1:2:1 $NaCl:CaCl_2:MgSO_4:Na_2SO_4$

[c] Calculated from data obtained when initial concentration (C_i) is 0.015 $\mu g \cdot g^{-1}$.

[d] Freundlich slope (N) significantly different ($P < 0.05$) from 1.

The Freundlich degree of nonlinearity (N) ranged from 0.87 to 1.08, indicating moderate to high sorption linearity. This range agrees with those identified in the literature, which spans from 0.77 to 1.08 in non-rice field soils.[30, 40-41] The overall sorption behavior of OXY in rice field soil can be described as highly linear with the majority of treatment groups (8 out of 10) possessing slopes statistically indistinguishable ($\alpha = 0.05$) from $N = 1$ (see Table 2.2). These results indicate that sorption of OXY to rice field soil is relatively concentration independent and binding site heterogeneity is low under the conditions tested.[13] While treatment groups had little impact on sorption N in general, significant differences ($\alpha = 0.05$) were observed when comparing the slopes between Biggs soil treatment at the highest incubation temperature (35°C) in 0.01 $CaCl_2$ and rice field salinities (Table 2.2). For Biggs soils, a decrease in N with incubation temperature was observed, with N being statistically distinguishable ($P < 0.0001$) from 1 at the highest temperature treatment (35 °C). According to the dual-mode sorption model, increased temperatures are associated with increased diffusion into SOM matrix where the distribution of binding site energy has greater heterogeneity.[37] As N has been shown mathematically to be an index of site energy distribution, with smaller N values indicating broader energy distribution, enhanced diffusion into the SOM aided by increased incubation temperatures may explain the observed trend for the Biggs soils.[42] Increasing temperature is also hypothesized to increase linearity (higher N) by disrupting micropore structures and decreasing binding site heterogeneity as SOM gradually transitions into a more expanded (rubbery) state.[37] This creates a dynamic relationship between temperature and N, where competing mechanisms offset each other, and the overall impact is dependent on the thermal response and properties of the SOM. Thus, multiple contributing factors may be involved across treatments and attribution to any one mechanistic rationale is not feasible.

Sorption $\log(K_F)$ ranged from 2.92 to 3.44. These values are greater than those reported in the literature for non-rice field soils (1.23 – 2.36), indicating the sorptive affinity of these rice field soils for OXY may be greater than other soils.[30, 40, 43] No statistical differences ($\alpha = 0.05$) were found between any treatments for sorption $\log(K_F)$ and no trends with temperature were identified. These results suggest that the sorption affinity of OXY to the soils are similar under the array of soils and rice field conditions tested.

2.4.3 Soil Desorption

Desorption Freundlich parameters by treatment are summarized in Table 2.3. OXY was poorly desorbed from soils, with percent desorption ranging from 9.3% to 27.0% with an average (±SE) of 15.5 ± 0.5%. In general, desorption of OXY from soils is reported to be highly hysteretic with very little desorption under both experimental and field studies.[29, 38, 40] In a field dissipation experiment in Indian subtropical soil, a similar desorption range was observed, ranging from 0.38 to 35.2% of the applied quantity.[29] As OXY exhibits both high sorption affinity and poor desorption potential, it will likely accumulate and persist in soil, rendering it less bioavailable to microbial degradation.[1] Although dissolved concentrations are likely to be low, soil erosion and transport via runoff will likely transport bound OXY to other aquatic sites where it may accumulate in the sediment.

Table 2.3 Freundlich Parameters for Desorption of OXY in California Rice Field Soils[a,b]

soil	Temp. (°C)	salinity (M)	$\log(K_{oc})^c$ ± SE	N ± SE	$\log(K_F)$ ± SE	R^2
Davis	15	0.01 $CaCl_2$	5.10 ± 0.02 a	0.99 ± 0.03 a	3.47 ± 0.08 a	0.998
	25	0.01 $CaCl_2$	5.15 ± 0.06 abc	0.94 ± 0.03 ab	3.36 ± 0.07^d a	0.997
	35	0.01 $CaCl_2$	5.34 ± 0.02 bc	0.91 ± 0.04 abc	3.43 ± 0.10 a	0.997
	25	0.01 RFS	5.15 ± 0.02 ac	1.11 ± 0.01 abc	3.83 ± 0.25^d a	0.963
	25	0.05 RFS	5.07 ± 0.02 a	0.83 ± 0.07 abc	3.03 ± 0.16 ab	0.992
Biggs	15	0.01 $CaCl_2$	5.28 ± 0.03 abc	0.74 ± 0.12 abc	2.80 ± 0.29 ab	0.963
	25	0.01 $CaCl_2$	5.54 ± 0.02 b	0.89 ± 0.09 abc	3.32 ± 0.22 ab	0.963
	35	0.01 $CaCl_2$	5.60 ± 0.12 abc	0.85 ± 0.02^e bc	3.32 ± 0.06^d a	0.997
	25	0.01 RFS	5.35 ± 0.07 abc	1.13 ± 0.11 abc	3.86 ± 0.29^d ab	0.966
	25	0.05 RFS	5.29 ± 0.03 abc	0.78 ± $0.03^{d,e}$ c	2.92 ± 0.08^d b	0.994

[a] Letters indicate statistically significant differences between treatments. Values with the same letter are not significantly different, while those with different letters are statistically distinct ($\alpha = 0.05$).
[b] Abbreviations: oxyfluorfen (OXY), temperature (Temp.), rice field salinity (RFS) with molar ratio of 10:1:2:1 $NaCl:CaCl_2:MgSO_4:Na_2SO_4$
[c] Calculated from data obtained when initial concentration (C_i) is 0.015 $\mu g \cdot g^{-1}$.
[d] Significant difference ($P < 0.05$) between sorption and desorption Freundlich parameter.
[e] Freundlich slope (N) significantly different ($P < 0.05$) from 1.

Desorption $\log(K_{oc})$ was higher than sorption $\log(K_{oc})$ for each treatment group and ranged from 5.07 to 5.60. Desorption $\log(K_{oc})$ for the Biggs soil was also greater than Davis soil for all treatments (Table 2.3). The observed increase in desorption K_{oc} and low percent desorption are consistent with desorption generally being an activated process, where a molecule must surpass a potential energy barrier greater than or equal to the free energy change (ΔG) for sorption to the soil surface in order to release back into aqueous solution.[44] Desorption $\log(K_{oc})$ increased with temperature and a significant increase ($P = 0.00021$) was seen between the 15 and

35 °C $CaCl_2$ treatments in Davis soils. Other significant differences based on treatment interactions for desorption $\log(K_{oc})$ are identified in Table 2.3.

Desorption isotherms were well described by the transformed Freundlich model (R^2 0.963 – 0.998). Desorption N values were generally lower than those for sorption and ranged from 0.74 to 1.13. The only report located that characterized desorption nonlinearity used a distinct definition of desorption N; this will be expanded upon in the hysteresis section.[40]

Desorption $\log(K_F)$ ranged from 2.80 to 3.86. The majority of desorption isotherms display higher apparent sorption affinity, as indicated by $\log(K_F)$, in comparison to that of the corresponding sorption isotherms. These increases were statistically distinguishable ($P < 0.05$) for four of the observed occurrences and are considered a hallmark of sorption hysteresis in soil.[24]

$\log(K_F)$ and N for both sorption and desorption decreased with increasing RFS for all treatments, while $\log(K_{oc})$ decreased with increasing rice field salinity for the majority of treatments (Table 2.2 & Table 2.3). The effects of salinity on soil sorption are complex and a variety of competing mechanisms influence outcomes. Salting out effects are commonly observed for HOCs.[14-15, 33] On the other hand, competitive interaction between solutes for binding sites on soil surfaces can decrease sorption.[45] Aqueous salinity levels are also known to alter the conformation and size of humic substances as well as the expansion and collapsing of the interlayers of clay mineral fractions of soils.[46-47] Cation concentration and valency further moderate the degree and types of interactions that occur.[48] One or more of these factors has the potential to influence sorption affinity as well as binding site availability and heterogeneity. These dynamic mechanisms make it difficult to predict outcomes across varying chemicals, soils, and saline conditions with certainty. Under the rice field salinity conditions tested, however, factors reducing sorption to soil surfaces generally appear stronger than those enhancing it. Interestingly, the consistent decrease in N indicates that increased saline conditions may alter the heterogeneity of sorption binding sites accessed. It has been shown that even a small deviation in N can underly large contributions from hole-filling mechanisms, which play a crucial role in isotherm nonlinearity and sorption irreversibility.[37] This implies that variations in rice field salinity could impact sorption mechanism and reversibility through salinity induced changes to SOM structure.

2.4.4 Hysteresis

Calculated HI ranged from 0.47 to 2.25 and are presented in Table 2.4. A mid-range C_e value of 0.005 $\mu g \cdot mL^{-1}$ was also identified within the observed sorption and desorption isotherm ranges shared between all treatments and was selected to calculate a middle HI value for comparison. Graphs of hysteresis indices across the full range calculable from sorption and desorption isotherm data for each treatment are available in the Supporting Information (Figure S2.5).

Table 2.4 Hysteresis Indices for OXY Desorption from California Rice Field Soil at Specific Residual Solution Phase Concentrations (C_e)[a]

			lower		middle		upper	
soil	temperature (°C)	salinity (M)[b]	C_e (μg·mL^{-1})	hysteresis index[c]	C_e (μg·mL^{-1})	hysteresis index[c]	C_e (μg·mL^{-1})	hysteresis index[c]
Davis	15	0.01 $CaCl_2$	0.0026	1.17 (0.47–2.21)	0.005	1.04 (0.51–1.77)	0.0119	0.88 (0.26–1.79)
	25	0.01 $CaCl_2$	0.0024	0.91 (0.30–1.83)	0.005	0.95 (0.44–1.64)	0.0104	0.99 (0.36–1.89)
	35	0.01 $CaCl_2$	0.0017	0.80 (0.22–1.68)	0.005	0.61 (0.20–1.17)	0.0098	0.50 (0.00–1.25)
	25	0.01 RFS	0.0023	1.12 (0.43–2.16)	0.005	1.33 (0.70–2.19)	0.0074	1.44 (0.71–2.47)
	25	0.05 RFS	0.0025	0.79 (0.23–1.62)	0.005	0.73 (0.28–1.33)	0.0135	0.64 (0.10–1.44)
Biggs	15	0.01 $CaCl_2$	0.0029	1.44 (0.65–2.61)	0.005	1.09 (0.53–1.86)	0.0175	0.47 (-0.05–1.27)
	25	0.01 $CaCl_2$	0.0030	1.55 (0.79–2.65)	0.005	1.42 (0.76–2.33)	0.0099	1.26 (0.54–2.32)
	35	0.01 $CaCl_2$	0.0018	1.12 (0.45–2.08)	0.005	1.07 (0.51–1.83)	0.0088	1.04 (0.39–2.00)
	25	0.01 RFS	0.0031	2.06 (1.09–3.47)	0.005	2.16 (1.25–3.45)	0.0074	2.25 (1.26–3.69)
	25	0.05 RFS	0.0031	1.69 (0.84–2.94)	0.005	1.4 (0.74–2.33)	0.0129	0.92 (0.31–1.81)

[a] Lower and upper C_e selected based on observed residual solution phase concentrations for both sorption and desorption isotherms. A middle C_e value of 0.005 μg·mL^{-1} was selected for cross-treatment comparison.

[b] Abbreviations: oxyfluorfen (OXY), rice field salinity (RFS) with molar ratio of 10:1:2:1 NaCl:CaCl2:MgSO4:Na2SO4

[c] Simultaneous (lower, upper) confidence bounds (α = 0.05) indicated by parentheses. Bounds that do not include zero (0) indicate significant sorption-desorption hysteresis.

Of the 50 individual *HI* values calculated, 49 showed significant hysteresis (*HI* > 0; α = 0.05). Although hysteresis was not significant at the upper C_e for Biggs soil incubated at 15 °C with 0.01 M $CaCl_2$, it was significant at middle and lower C_e levels for that treatment, suggesting hysteretic processes predominate across all treatments and the majority of C_e conditions. Overall, hysteresis was greater in Biggs soils and observed to increase with decreasing residual solution phase concentration. This pattern of concentration-dependent hysteresis is consistent with the dual-mode model of sorption, which holds that the contribution of hole-filling mechanisms is greater at low concentrations.[37] Binding sites accessed through this mechanism are thought to account for hysteresis due to higher energy of binding and limited availability to sorbing molecules.[49] A decrease in *HI* with increasing RFS was also observed for both soils across all C_e (Figure S2.5), indicating hysteresis is sensitive to ionic strength and the degree of binding irreversibility may vary site-to-site based on individual rice field salinity conditions. Possible mechanisms that could explain this observation include competitive sorption with ions for high energy binding sites or changes in SOM structure at high salinity that limit diffusion into or within the SOM matrix.[49]

Few Freundlich isotherm studies are available in the literature for OXY and only a single study was located that characterized the degree of desorption nonlinearity and hysteresis in soil. In a batch equilibrium study in two Spanish soils, desorption of OXY was found to be highly hysteretic in both soils through calculation of another index used to characterize hysteresis known as the thermodynamic index of irreversibility (*TII*).[40] *TII* represents the difference in measured desorption state versus a hypothetically fully reversible state, with indices of 0 representing complete reversibility and trending towards 1 with complete irreversibility.[50] Methodology for calculation of *TII* are presented in the Supporting Information. *TII* calculated in the two Spanish soils ranged from 0.927 to 0.975 in sandy clay loam and silty clay loam, respectively, indicating high irreversibility of binding.

For comparison, *TII* were also calculated using the data produced in this investigation and are presented in the Supporting Information (Table S2.2 and Table S2.3). Calculated *TII* ranged from 0.128 to 0.915, indicating OXY binding to soil was mostly reversible to highly irreversible. However, the majority (86%) of the *TII* calculated were ≥ 0.75, with an average value of 0.80, suggesting that sorption to the soil is predominantly a highly irreversible process.[50] Calculated *TII* were also generally greater in treatments with Biggs soil and exhibited inverse concentration-dependency in a manner similar to *HI*. Overall, results for both indices agree and indicate the occurrence of pronounced sorption-desorption hysteresis under California rice field conditions.

Hysteretic processes can profoundly impact the overall fate of herbicides within the environment. Herbicides irreversibly bound to the soil are typically not bioavailable for microbial degradation, leading to persistence.[49] Resistance to entering the water column may further inhibit environmental half-lives as photolysis is the primary route of degradation for OXY.[6] Aging within the soil may result in further sequestration over time, although this diffusion-limited process may be impeded somewhat due to the high sorption affinity of OXY for soil.[37] While sorption results in this study suggest OXY will be found predominantly in rice field sediment, this extended aging profile may create longer periods where the labile fractions of OXY residues may be mobilized into overlying field water, especially when water turnover and dissolved/suspended organic matter levels are high. Once in the water column, OXY may be subject to transport off-field via runoff and erosion.

Accurate determination of herbicide mass balance in sediment and surface waters over time is paramount to predicting fundamental interests, such as effective water holding periods and risk to non-target organisms, particularly aquatic species highly susceptible to OXY toxicity. Factors modulating the partitioning behavior for OXY, such as rice field salinity and soil characteristics, must also be considered. Significant hysteresis is also anticipated in rice field soil and models that fail to incorporate this nonideal behavior are likely to provide estimates that differ markedly from reality. Thus, careful consideration of these principal factors will provide the foundation for making safe and effective decisions regarding the use of OXY as an herbicide in California rice fields.

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2.6 Supporting Information

SOM Removal for FTIR and XRD Analysis

Soil organic matter (SOM) was removed from soil samples via chemical oxidation according to the methods described by Margenot *et al.*[1] In brief, a solution of 6% w/v NaOCl (bleach) was adjusted to pH 9.5 by adding 1 M HCl dropwise while mixing. Twenty-five (25) mL of the bleach solution was added to 4 g soil (sieved <2 mm; air dried) in a 50-mL conical tube and mixed by sonication (600 s, output frequency 37 kHz, power 100%). The mixture was incubated in a hot-water bath (80 °C, 15 min) to increase the oxidation rate and then centrifuged (3452 *g*, 15 min). The supernatant was discarded, and the process was repeated two additional times. Twenty (20) mL of deionized H_2O (dH_2O) was then added to the soil and mixed for 6 minutes on a horizontal shaker (120 rpm), then centrifuged (3452 *g*, 15 min). This process was repeated two additional times. The remaining soil pellet was then extracted from the bottom of the centrifuge tube using a spatula and dH_20 into glass dish containers before oven drying (60 °C) for 48 hours. Once dried, the sample was subjected to FTIR and XRD analysis.

FTIR Analysis of SOM Content

Soil organic matter (SOM) content was analyzed via spectral subtraction using Fourier transform infrared (FTIR) spectroscopy.[2] FTIR spectra of native soil samples and soil samples with SOM removed were collected using diffuse reflectance infrared Fourier transform spectroscopy (DRIFT; PIKE Technologies EasiDiff) with soil (air dried) diluted to 10% with KBr.[3] All FTIR spectra were collected using a Thermo Nicolet 6700 FTIR spectrometer (Thermo Scientific) using 400 scans, 4 cm^{-1} resolution, and a DTGS detector. Results of the analysis are presented in Figure S2.1.

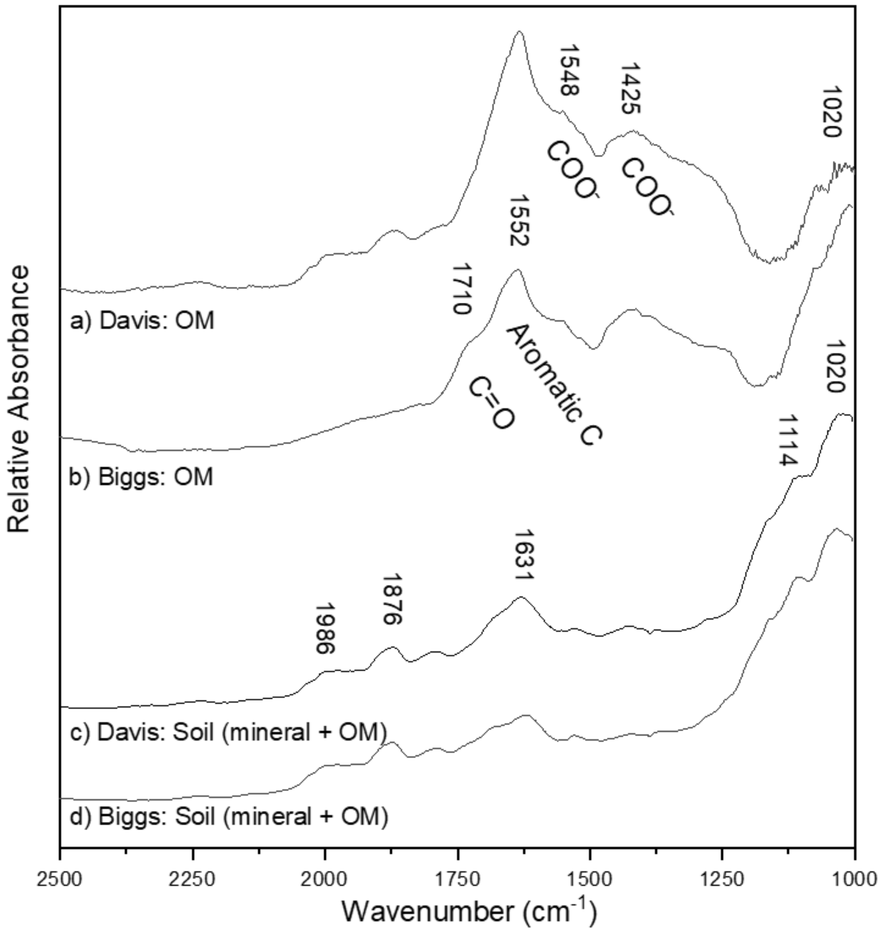

Figure S2.1 DRIFT Spectra of organic matter (OM) fraction of a) Davis and b) Biggs soils. Spectra c) and d) are provided for comparison to the unaltered soil samples. Selected peak wavenumbers are provided, with regions of important organic functional groups identified.

XRD Analysis of Soil Mineralogy

The primary and secondary mineral composition of the Davis and Biggs soils were identified using X-ray diffraction (XRD).[4] First, the samples for mineralogical analysis underwent an additional organic matter removal pretreatment process that included the use of a 5% NaOCl solution that was pH adjusted to 9 with HCl. Briefly, the samples were mixed with the 5% NaOCl solution, heated on a water bath for 30 minutes, certified for 30 minutes. The process was completed three times before drying. Soil samples (<2mm) were then ground and homogenized to a <50 µm homogenous bulk powder using tungsten carbide grinding vessels and balls on a Retsch MM500 Vario Mixer Mill. Samples for clay mineralogical analysis were prepared as oriented clay mounts on glass slides using an established vacuum filtration approach that included the standard suite of chemical and heat treatments for sample preparation: KCl-saturation, heat-treated KCl (550°C, 300°C), Mg-saturation, and overnight Mg/glycerol solvation.[5]

The randomly oriented bulk powder mounts and the oriented clay mounts were analyzed with a Bruker D8 Advance Multi-Purpose X-Ray Diffractometer (Bruker, Karlsruhe, Germany) which produces X-rays with an accelerating potential of 40 kV, a current of 40 mA, and a LynxEye-2 solid state linear array detector with a Ni-filter. The randomly oriented powder mounts were measured from 5 to 70 2-theta with a step size of 0.021 °, a dwell time of 2 s on a spinner sample stage with a 1s rotation time. The oriented clay mounts were analyzed with a scan range of 3-30 degrees 2-theta, a step size of 0.021 °, and a dwell time of 2 s.

A semi-quantitative phase analysis method was employed using Bruker's DIFFRAC.EVA (Version 6.0) software to identify the mineral assemblages in the randomly oriented powder mounts and by using reference mineral patterns from the Crystallography Open

Database (Minerals, rev. 266484; Bruker, Madison, WI). Results of the analysis are presented in Figure S2.2.

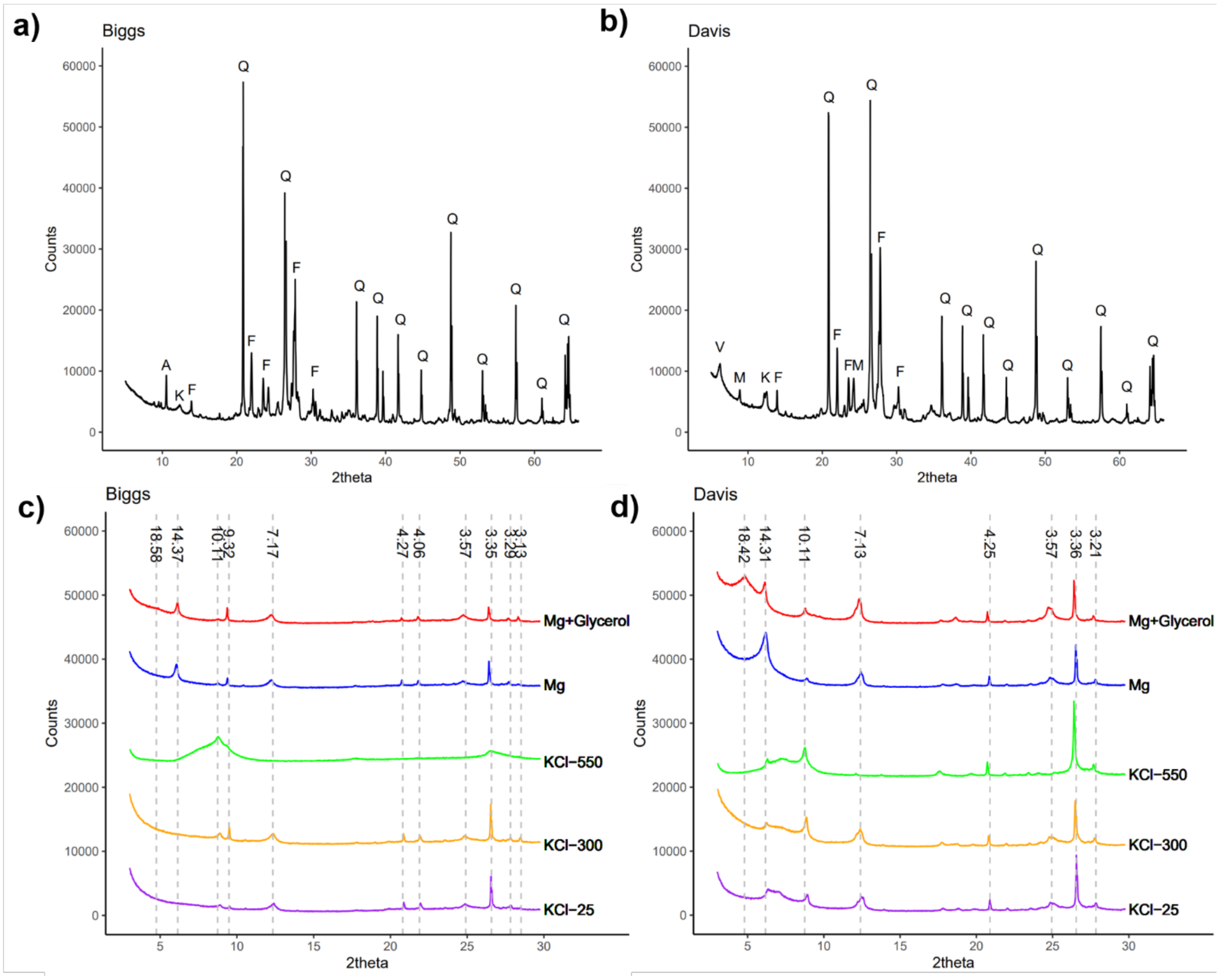

Figure S2.2 X-Ray Diffractogram patterns for randomly oriented soil samples from a) Biggs and b) Davis. Oriented sample mounts of the soil clay fractions were also analyzed following preparation using established chemical and heat treatments for c) Biggs and d) Davis. Capital letters in a) and b) correspond to minerals identified in the samples where A = Amphibole, F = Feldspar, K = Kaolinite, M = Mica, and Q = Quartz. The vertical dashed lines and numbers correspond to the d-spacing for each peak identified in c) and d).

Table S2.1 Mass Spectrometer Acquisition Parameters[a]

Scan Segments	Compound	Precursor Ion ($m \cdot z^{-1}$)	Product Ion ($m \cdot z^{-1}$)[b]	Fragmentor (V)	CE (V)	Cell Accelerator Voltage (V)	Polarity
1	d5-OXY	367	**237**	106	28	4	Positive
2	OXY	362	**316**	106	12	4	Positive
3	OXY	362	237	106	28	4	Positive

[a] Abbreviations: oxyfluorfen (OXY), d5-oxyfluorfen (d5-OXY), collision energy (CE)

[b] Bold product ions used for quantitation of compound

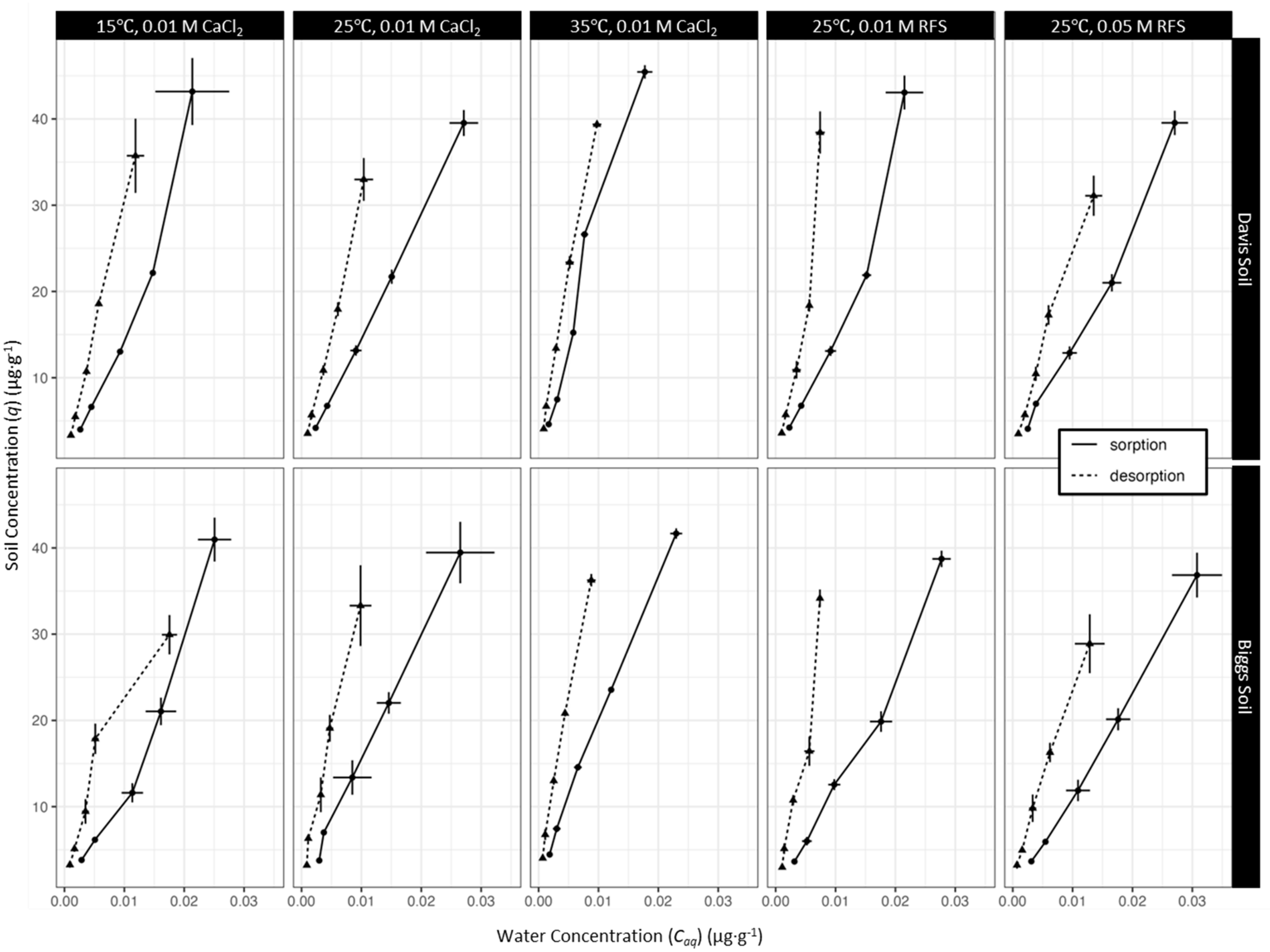

Figure S2.3 Untransformed Freundlich isotherms on treatment averaged C_{aq} and q values (across replicates) with error bars in both C_{aq} and q values (standard deviation across replicates) for sorption and desorption of OXY to California rice field.

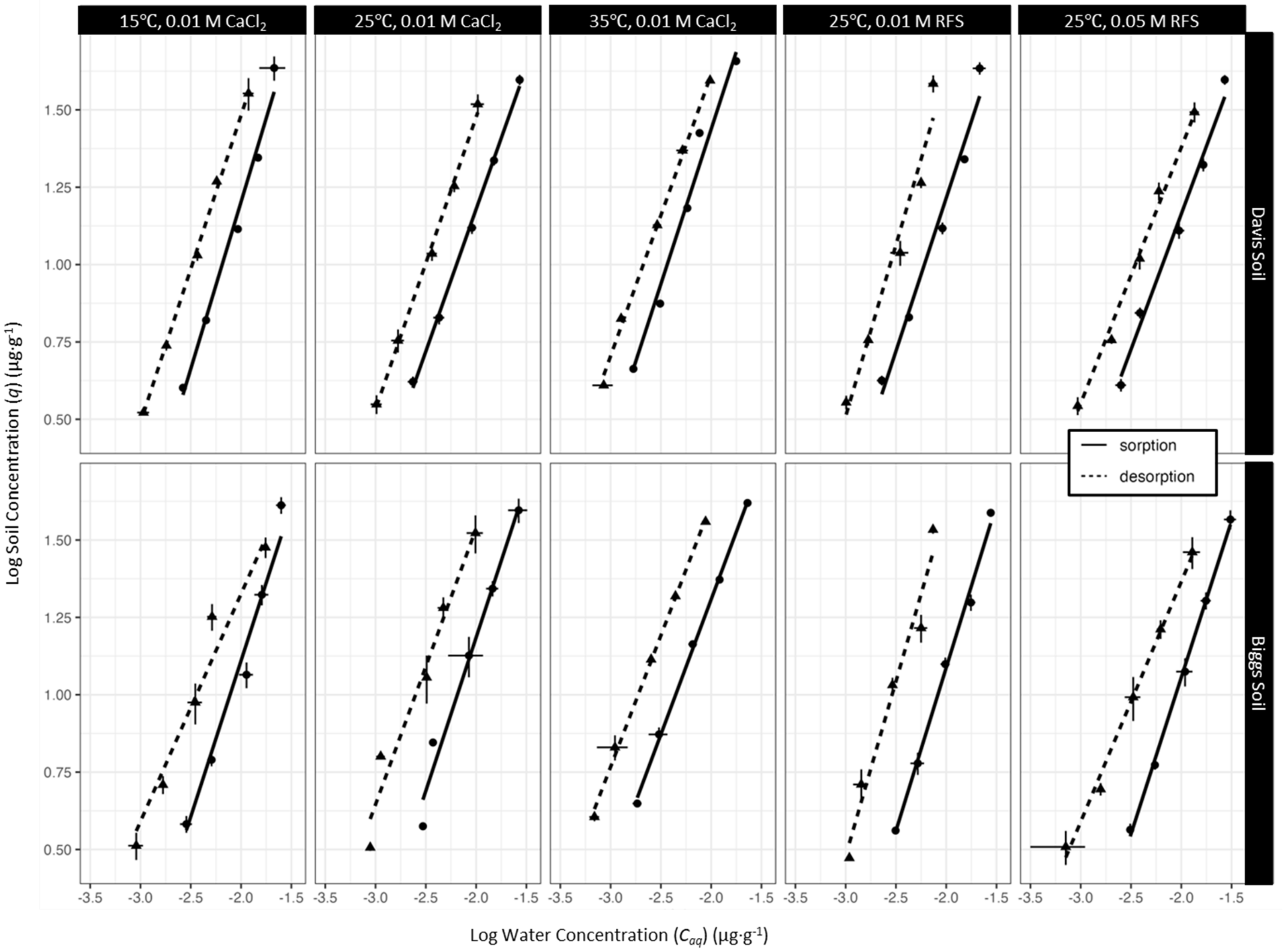

Figure S2.4 Log transformed Freundlich isotherms on treatment averaged C_{aq} and q values (across replicates) with error bars in both C_{aq} and q values (standard deviation across replicates) for sorption and desorption of OXY to California rice field.

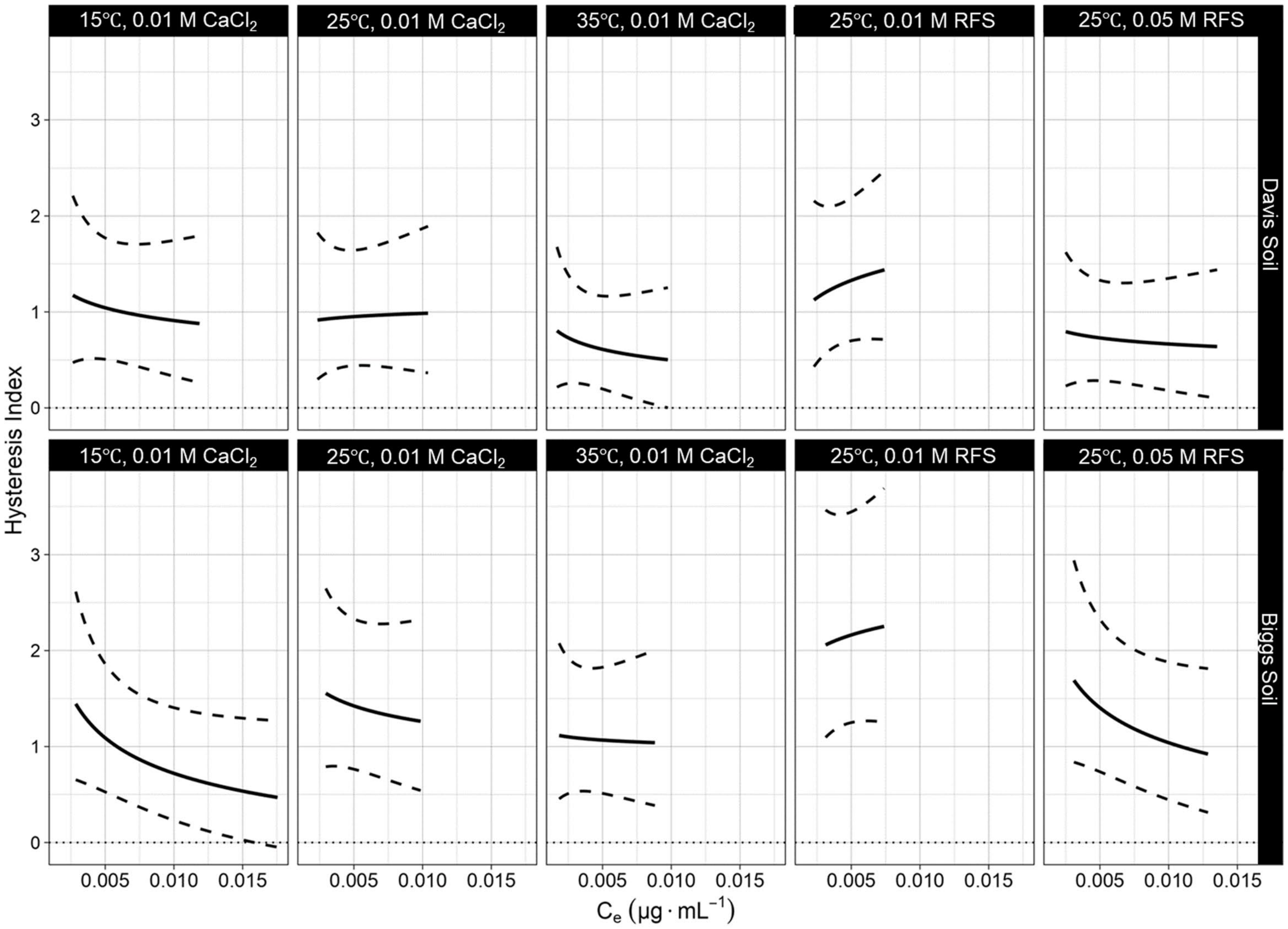

Figure S2.5 Hysteresis indices by residual solution phase concentration, C_e, with simultaneous confidence bounds ($\alpha = 0.05$)

Thermodynmic Index of Irreversibility (TII)

The degree of sorption hysteresis was quantified through calculation of the thermodynamic index of irreversibility (TII) according to the equation (S2.1) below:

$$TII = 1 - \frac{N_{desorb}}{N_{sorb}} \tag{S2.1}$$

where N_{sorb} is the Freundlich exponent for the sorption branch and N_{desorb} is the Freundlich exponent along the desorption branch measured across one or more successive desorption steps within the same reaction vessel.[6] Values for N_{sorb} are presented in Table 2.2 of the primary manuscript while N_{desorb} according to the definition above is presented below in Table S2.2, with each desorption branch characterized by a single desorption step at a specific initial concentration. Calculated TII are presented in Table S2.3 by initial concentration for each treatment.

Table S2.2 N_{desorb} Values for OXY Desorption from California Rice Field Soils by Initial Concentration (C_i)[a]

soil	**temperature (°C)**	**salinity (M)[a]**	**C_i (µg·mL^{-1})**				
			0.009	**0.015**	**0.03**	**0.05**	**0.09**
Davis	15	0.01 $CaCl_2$	0.204	0.207	0.210	0.186	0.322
	25	0.01 $CaCl_2$	0.201	0.181	0.210	0.210	0.189
	35	0.01 $CaCl_2$	0.181	0.125	0.184	0.331	0.240
	25	0.01 RFS	0.200	0.181	0.188	0.176	0.107
	25	0.05 RFS	0.156	0.310	0.230	0.193	0.347
Biggs	15	0.01 $CaCl_2$	0.140	0.167	0.176	0.143	0.878
	25	0.01 $CaCl_2$	0.131	0.087	0.168	0.127	0.171
	35	0.01 $CaCl_2$	0.102	0.095	0.119	0.122	0.145
	25	0.01 RFS	0.193	0.121	0.128	0.166	0.095
	25	0.05 RFS	0.086	0.145	0.160	0.204	0.279

[a]Abbreviations: Desorption branch Freundlich exponent (N_{desorb}); Oxyfluorfen (OXY); Initial concentration (C_i); Rice field salinity (RFS) with molar ratio of 10:1:2:1 $NaCl:CaCl_2:MgSO_4:Na_2SO_4$

Table S2.3 TII Values for OXY Desorption from California Rice Field Soils by Initial Concentration (C_i)[a]

soil	temperature (°C)	salinity (M)[a]	C_i (µg·mL^{-1})				
			0.009	**0.015**	**0.03**	**0.05**	**0.09**
Davis	15	0.01 $CaCl_2$	0.811	0.808	0.806	0.827	0.702
	25	0.01 $CaCl_2$	0.781	0.803	0.772	0.772	0.794
	35	0.01 $CaCl_2$	0.819	0.875	0.816	0.669	0.760
	25	0.01 RFS	0.798	0.817	0.810	0.822	0.892
	25	0.05 RFS	0.822	0.647	0.737	0.780	0.604
Biggs	15	0.01 $CaCl_2$	0.861	0.834	0.825	0.858	0.128
	25	0.01 $CaCl_2$	0.868	0.912	0.831	0.872	0.827
	35	0.01 $CaCl_2$	0.883	0.891	0.863	0.860	0.834
	25	0.01 RFS	0.817	0.885	0.878	0.842	0.910
	25	0.05 RFS	0.915	0.857	0.841	0.798	0.725

[a] Abbreviations: Thermodynamic Index of Irreversibility (TII); Oxyfluorfen (OXY); Initial concentration (C_i); Rice field salinity (RFS) with molar ratio of 10:1:2:1 NaCl:$CaCl_2$:$MgSO_4$:Na_2SO_4

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Chapter 3 |

Predicting Air-Water Partitioning of Oxyfluorfen Under California Rice Field Conditions: An Approach for Broader Application

David J. Bonnar and Ronald S. Tjeerdema

3.1 Abstract

The objective was to determine Henry's law constants (K_H) for oxyfluorfen [OXY; 2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl)benzene] at California rice field temperatures (5 to 40 °C). This was accomplished by first developing a screening method to evaluate the feasibility of experimental measurement of K_H via the gas-stripping method (GSM). Results indicated that K_H cannot be feasibly determined via GSM and must be calculated. Thus, K_H was calculated using four air-water partitioning models: (1) EPI Suite, (2) Kühne (3) AQUAFAC-Sepassi, and (4) two-point extrapolation (TPE) models. Results for EPI Suite, Kühne, and TPE models indicated OXY is slightly volatile (K_H 3.00E-07 – 1.00E-05 $\text{atm}\cdot\text{m}^3\cdot\text{mol}^{-1}$), except at low temperatures (5 – 10 °C) where it is nonvolatile ($K_H <$ 3.00E-07 $\text{atm}\cdot\text{m}^3\cdot\text{mol}^{-1}$). In contrast, the AQUAFAC-Sepassi model suggested substantial volatility ($K_H >$ 1.00E-05 $\text{atm}\cdot\text{m}^3\cdot\text{mol}^{-1}$) under all temperatures evaluated. However, further investigation revealed limitations in the ability of the model to predict key physical properties for OXY, suggesting less reliable results. Thus, OXY is expected to be nonvolatile to slightly volatile in California rice fields.

3.2 Introduction

Oxyfluorfen (OXY, trade name Goal) is a broad-spectrum, diphenyl ether herbicide and one of the most widely applied pesticides in California.[1] With the recent development of OXY-tolerant rice strains, efforts are underway to expand its use to include California rice fields.[2] Not currently registered for use in rice and historically prohibited for use in or near aquatic resources due to aquatic toxicity, its fate in rice fields is poorly understood.[3-4]

Air-water partitioning is one of the primary fate processes in rice fields, with volatilization from water bodies recognized as a potentially significant dissipation route for recalcitrant herbicides such as OXY.[5-6] The key physical property used to predict air-water partitioning behavior is the Henry's law constant (K_H). K_H is an equilibrium partitioning coefficient expressing the relative volatility of a compound and is temperature dependent.[7] As field water temperatures are known to vary considerably, with observed fluctuations ranging from 5 to 38 °C, it is important to consider its influence on K_H when predicting the fate of OXY.[8-9]

To our knowledge, there are no experimentally measured values for K_H currently available for OXY. However, K_H has been calculated at 25 °C, with estimates ranging from 2.35E-07 to 1.50E-06 $\text{atm}\cdot\text{m}^3\cdot\text{mol}^{-1}$.[10-12] Although reported to be nonvolatile based on these estimates, OXY has been observed to co-distill from moist soils.[6, 13-15] Furthermore, K_H values estimated from physical-chemical properties are also typically less reliable than experimentally-derived values as errors incurred during measurement of properties are compounded when calculating K_H.[16] The effects of temperature may also alter volatility.[7] Thus, considerable uncertainty exists regarding the air-water partitioning behavior of OXY under California field temperatures.

The traditional method for experimental determination of K_H of hydrophobic organic chemicals (HOCs) is the gas-stripping method (GSM).[5] However, this method fails for HOCs possessing both low vapor pressure and poor water solubility, such as OXY.[16-18] These characteristics lead to slow volatilization rates, limiting the sensitivity of the method, and can favor extensive sorption to apparatus walls, invalidating results. Such failures are costly and may lead to erroneous conclusions if ignored. Thus, there is a need to evaluate the suitability of the GSM for OXY prior to conducting potentially inviable experiments.

If experimental determination is infeasible, air-water partitioning models can be used to calculate K_H. Methods employed by these models encompass strategies such as surrogate use, correlating chemical structures with physical properties, and interpolating/extrapolating from existing data.[7, 19-20] These diverse approaches reflect distinct assumptions about the factors influencing partitioning behavior. As such, models may disagree on outcomes and reliance on a single model increases the risk of reaching conclusions that differ markedly from reality. Thus, multiple models should be considered and compared, both to each other and available data, to evaluate performance.

The objective of this study was to determine K_H for OXY at California field temperatures (5 to 40 °C). Both empirical and estimation methods for predicting air-water partitioning behavior for HOCs were considered and compared. A simple screening method was developed to evaluate the feasibility of experimental determination of K_H via the GSM. Four air-water partitioning models were selected for calculation of K_H at the temperatures of interest: (1) EPI Suite, (2) Kühne, (3) AQUAFAC-Sepassi, and (4) two-point extrapolation (TPE) models. The advantages and limitations of each model were evaluated, and their results compared.

3.3 Methods

3.3.1 GSM Feasibility Evaluation

The feasibility of measuring K_H via gas stripping was evaluated by estimating the amount of time required to isothermally strip a specified fraction of solute from water phase using gas flow through. This estimated duration was then compared to experimental time benchmarks, beyond which K_H measurement would be considered infeasible (discussed below). This evaluation is conceptualized based on the traditional GSM wherein a gas-stripping apparatus filled with a specific volume of solute-containing water is purged with gas to strip solute from the water column into vapor phase. K_H is calculated by measuring the decrease in aqueous concentration of the solute over time as gas is purged through the water column and is given by equation (3.1):

$$\ln(\frac{C_{w,t}}{C_{w,0}}) = -\frac{K_H \cdot F_{gas}}{V_w \cdot RT} \cdot t \tag{3.1}$$

where $C_{w,0}$ is the initial aqueous concentration, $C_{w,t}$ and aqueous concentration at time t, K_H is the Henry's law constant, F_{gas} is the purge gas flow rate, V_w is the volume of aqueous phase, R is the ideal gas constant, T is temperature, and t is time.[5] The fraction of solute remaining is expressed by the ratio of $C_{w,t}$ to $C_{w,0}$ and the fraction of solute stripped is its mathematical complement, as expressed in equation (3.2):

$$\frac{C_{w,t}}{C_{w,0}} = 1 - f_{strip} \tag{3.2}$$

where f_{strip} is the fraction of solute stripped from the aqueous phase. Thus, the amount of time required to strip a target fraction of solute, t_{strip}, is expressed by equation (3.3):

$$t_{strip} = -\,ln(1 - f_{strip}) \cdot \frac{RT}{K_H} \cdot \frac{V_w}{F_{gas}} \tag{3.3}$$

This equation was used to estimate amount of time, t_{strip}, to strip a specified fraction of solute from the water phase, f_{strip}.

The sensitivity of the GSM relies directly on the ability to characterize the slope of the decrease in aqueous concentration over time.[16] Thus, a substantial decrease in aqueous concentration is required for accurate determination of K_H. For purposes of this screening-level evaluation, a 20% reduction in aqueous phase concentration (f_{strip}= 0.2) was selected as the minimal amount sufficient for accurate calculation of K_H. As chemicals exhibiting ideal behavior experience minimal sorption and extensive volatilization (>90% reduction in aqueous phase concentration), this target reduction is considered a "best-case scenario" where the method is sufficiently sensitive to provide an accurate determination under these minimal loss conditions.[16] Selected temperature, volume of water, and gas flow rate were 25 °C (298.15 K), 1.5 L, and 0.05 $L\cdot min^{-1}$, respectively. K_H was estimated according to equation (3.4):

$$K_H = \frac{VP}{S_w} \tag{3.4}$$

where VP and S_w are the vapor pressure and water solubility. Selected vapor pressure and water solubility for calculation of K_H at 25 °C were 4.66E-10 atm and 0.116 $mg\cdot L^{-1}$, respectively.[11]

A major impedance to experimental measurement of K_H via GSM is the stability of the analyte. As decrease in aqueous concentration is the primary measurement used to calculate K_H, degradation exceeding negligible amounts (e.g., <1%) may lead to inaccurate characterization of K_H. Furthermore, the lack of significant degradation is one of the core assumptions underlying the development of equation (3.1).[16] Thus, the first criterion used to evaluate feasibility was to compare the estimated time to conduct a gas stripping experiment (t_{strip}) against the expected aqueous half-life for OXY. Potential routes contributing towards degradation in aqueous solutions include hydrolysis, photolysis, and aerobic microbial metabolism. Basic experimental controls, such as water filtration and covering glassware to prevent light exposure, are typically sufficient to protect against the effects of photolysis and microbial metabolism. Hydrolysis is less easily controlled, however, and remains a relevant degradation pathway during gas stripping experiments. Thus, the literature was reviewed for hydrolysis half-life (λ_{hyd}) for OXY. If t_{strip} > λ_{hyd}, experimental determination of K_H via GSM was considered infeasible.

Experimental stability also becomes a greater issue with prolonged gas stripping periods. Evaporation of aqueous phase over-time progressively becomes a concern and sorption to container glassware may be exacerbated. Other practical considerations, such as cost, time, and the need for active monitoring and maintenance of experimental conditions places limits on experimental feasibility. Thus, we suggest as a second criterion that experimental durations be limited to no more than 30 days and considered experimental measurement of K_H infeasible if calculated t_{strip} was greater than 30 days.

3.3.2 Air-Water Partitioning Models

Four air-water partitioning models, described below, were selected to calculate K_H at relevant rice field temperatures (5 to 40 °C). For each model, the natural logarithm of K_H was plotted against inverse temperature to yield a linear van't Hoff plot in the form of equation (3.5):

$$\ln K_H = -\frac{A}{T} + B \tag{3.5}$$

where A (Kelvin) is the slope and B (-) is the intercept [21]. The slope A of the regression line was then used to determine $\Delta_{aw}H$ through equation (3.6):

$$\Delta_{aw}H = A \cdot R \tag{3.6}$$

where $\Delta_{aw}H$ is the enthalpy of transfer from air to water ($\mathrm{kJ \cdot mol^{-1}}$) and R is the gas constant ($\mathrm{kJ \cdot mol^{-1} \cdot K^{-1}}$). $\Delta_{aw}H$ serves as an important input parameter for rice field fate models, such as the Pesticides in Flooded Applications Model (PFAM), and can be used to extrapolate the magnitude of change in K_H with temperature if known.[21-22]

3.3.2.1 EPI Suite

The Estimation Program Interface (EPI) Suite v4.11 is a physical/chemical property and environmental fate estimation program developed by the U.S. Environmental Protection Agency and Syracuse Research Corp.[20] It is bundled with the PHYSPROP database which contains chemical structures, names, and physical properties for over >40,000 chemicals. It has undergone detailed review by the US. Environmental Protection Agency's independent Science Advisory Board and is capable of estimating and extrapolating environmental fate properties based on the available data and peer reviewed science.[23]

EPI Suite was used to calculate K_H variation with temperature via its HENRYWIN subprogram. In brief, a similar compound slope analogy method is applied by the program to derive values for A and B in equation (3.5), allowing for calculation of K_H as a function of temperature. The selected chemical is assigned a chemical class for which empirical slope correlation data are available. This class is used to determine a surrogate slope value A for the chemical and is considered applicable to predicting variations in temperature between 0 and 50 °C. The intercept, B, is then determined by the model by referencing experimental values in its database for K_H at 25 °C. If experimental data are not available, the program estimates K_H based on available vapor pressure and water solubility data.

3.3.2.2 Kühne Model

The model developed by Kühne, et al. (Kühne model) is an integrated quantitative structure-property relationship (QSPR) model that predicts slope A based on functional group contribution.[19] When an estimate of K_H for at least one temperature is available, K_H may be extrapolated at other temperatures according to equation (3.7):

$$\ln K_H = K_{H,0} - A(\frac{1}{T} - \frac{1}{T_0}) \tag{3.7}$$

where K_H is the Henry's law constant at the temperature of interest, $K_{H,0}$ is the Henry's law constant at the reference temperature, T is temperature, and T_0 is the reference temperature. For purposes of this analysis, $K_{H,0}$ was calculated at 25 °C via equation (3.4) using available vapor pressure and water solubility data.

3.3.2.3 AQUAFAC-Sepassi Model

A composite model composed of two component QSPR models was used to calculate K_H through independent calculation of water solubility and vapor pressure at each temperature. The model described by Sepassi, et al. was used to calculate vapor pressure at each temperature according to equation (3.8):

$$\log VP = -\frac{(50 - 19.1\log(\sigma) + 7.4\tau)(T_m - T)}{2.3RT} - \frac{(86 + 0.4\tau + 1421HBN)(T_b - T)}{2.3RT} + \frac{(-91 - 1.2\tau)}{2.3R} \cdot \left[\frac{T_b - T}{T} - \ln\left(\frac{T_b}{T}\right)\right] (atm) \tag{3.8}$$

where VP is vapor pressure (atm), σ is rotational symmetry, T_m and T_b are the melting and boiling points, τ is the effective number of torsional bonds, HBN is the hydrogen bond density number, R is the universal gas constant (J·mol^{-1}·K^{-1}), and T is temperature.[24] Water solubility at each temperature was estimated by the Aqueous Functional Group Activity Coefficients (AQUAFAC) group contribution method as described in equation (3.9):

$$\log S_w = -0.01(T_m - T) - \sum nq \tag{3.9}$$

where S_w is solubility in water (mol·L^{-1}), q is the contribution value of the AQUAFAC group, and n is the frequency of occurrence of the group.[25] K_H was then calculated via equation (3.4) at each temperature. For purposes of this analysis, this composite QSPR model is referred to as the AQUAFAC-Sepassi model. Although this model has not been validated, the same approach has been previously used to calculate K_H at rice field temperatures for chlorantraniliprole.[26]

3.3.2.4 TPE Model

The linear nature of the van't Hoff relation allows for calculations of the regression parameters, A and B, provided K_H is available for at least two different temperatures.[7] In this study, this approach is referred to as the two-point extrapolation (TPE) model. K_H was calculated via equation (3.4) at 20 and 25 °C using available vapor pressure and water solubility data. Calculated K_H and temperatures were then plotted via equation (3.5) and regressed to interpolate parameters, A and B. The regression parameters were then used to extrapolate K_H across the temperatures evaluated via equation (3.5).

3.4 Results and Discussion

3.4.1 GSM Feasibility Evaluation

Calculated t_{strip} was 78 days, based on an estimated K_H of 1.45E-06 atm·m^3·mol^{-1} and selected f_{strip} of 0.20. OXY was determined to be stable to hydrolysis.[3] Thus, OXY passes the first feasibility criterion and degradation via this pathway alone is considered unlikely to pose significant issues when measuring K_H via GSM. However, OXY was found to undergo relatively rapid aqueous photolysis, with reported half-lives ranging from 5.5 hours to 7.5 days depending on lighting conditions.[27-28] OXY may also be degraded by aerobic aquatic metabolism, with half-lives ranging from 16.0 to 39.6 days.[11] If considered in this assessment, the speed with which OXY degrades via these pathways would be sufficient grounds for rejecting GSM feasibility. Thus, proper controls (e.g., water filtration; sterile glassware; light-protective coverage) are important to prevent unexpected losses that might impact K_H measurement.

Compounds that fail to pass the first feasibility criteria are expected to degrade by 50% or more by the end of the experiment. While unaccounted losses of this degree reasonably invalidate results, thresholds for negligible degradation (e.g., 1% degraded) can be selected to adopt a less permissive benchmark. If the aqueous rate is known, this benchmark time can be calculated via the appropriate regression equation for the reaction order. For compounds susceptible to pH-dependent hydrolysis, the feasibility criteria proposed in this paper should be applied at each pH of interest, which is typically studied within the range (6.5 – 8.5) of natural waters.[29]

Although the potential for aqueous degradation does not pose a major feasibility concern for OXY, the estimated time to perform the experiment (78 days) exceeds the suggested limit of 30 days. Thus, OXY does not pass the second criterion and experimental measurement of K_H via GSM is considered infeasible due to experimental stability concerns and practical considerations. Progressive loss of aqueous phase due to evaporation is unavoidable, ultimately placing limits on the maximum duration of gas stripping experiments. Sorption to glassware is also well-known to create substantial barriers to accurate measurement of partitioning coefficients for HOCs, such as OXY, and the total amount sorbed tends to increase with time.[30-31] Sorbed solute may also become more resistant to desorption from glassware over time, leading to increased risk of contamination and irrecoverable loss of analyte.[31]

An investigation into the air-water partitioning of polybrominated diphenyl ethers (PBDEs) found extensive sorption to glassware by the more hydrophobic congeners, with up to 68% of the total applied mass being sorbed.[16] This degree of sorption was sufficient to invalidate the GSM for these hydrophobic diphenyl ethers. The authors also developed an integrated gas-stripping method (IGSM) to circumvent this limitation by measuring and accounting for the sorbed amount. However, results for this method were found to be erratic for hydrophobic PBDEs. This variation was hypothesized to be driven by the slow loss of chemical from aqueous phase, rendering measurement of smaller rate constants less accurate. The additional time and effort required to implement the IGSM places further limitations on this method as a suitable alternative to the GSM for OXY and does not fully address the totality of feasibility concerns.

Depending on the sensitivity of the method, a 20% reduction in aqueous phase concentration may be insufficient for accurate determination of K_H and a higher f_{strip} may be required. However, increases in target f_{strip} may increase the experimental duration, t_{strip}, by a substantially greater amount as their relationship is non-linear and asymptotic as expressed in equation (3.3). For example, if a target f_{strip} of 0.50, 0.75, or 0.90 were selected for OXY, the estimated t_{strip} would be 243, 487, and 808 days, respectively. These longer experimental durations drive up costs, demand longer periods of active monitoring, and compromise the long-term stability of the experiment for the reasons aforementioned.

Given that the selected f_{strip} value for modeling (0.20) and presumption of no substantial sorption to container walls represent potentially overly optimistic experimental conditions, surpassing the benchmark time criteria for t_{strip} (30 days) should be regarded as a prohibitive constraint on experimental feasibility. Thus, calculation of K_H for OXY is recommended over experimental measurement.

3.4.2 Air-Water Partitioning Models

3.4.2.1 Results Summary

Calculated K_H by temperature for selected models are presented in Table 3.1. Fully parametrized models, data, and results for this assessment are available in Electronic Supporting Information 1 (ESI1; https://doi.org/10.6084/m9.figshare.24778371). Calculated K_H at 20 and 25 °C were 9.52E-07 and 1.45E-06 $atm \cdot m^3 \cdot mol^{-1}$, respectively, based on literature reported vapor pressure and solubility values of 2.63E-10 atm and 0.1 $mg \cdot L^{-1}$ at 20 °C, respectively, and 4.66E-10 atm and 0.116 $mg \cdot L^{-1}$ at 25 °C, respectively.[3, 11, 32]

Table 3.1. Calculated Henry's Law Constants (*K_H*) by Temperature for Selected Models

Temperature (°C)	K_H (atm·m^3·mol^{-1})			
	EPI Suite	Kühne	AQUAFAC -Sepassi	TPE
5	2.18E-07	1.39E-07	1.92E-05	2.45E-07
10	3.09E-07	2.58E-07	4.08E-05	3.91E-07
15	4.32E-07	4.68E-07	8.41E-05	6.15E-07
20	5.99E-07	8.33E-07	1.68E-04	9.52E-07
25	8.20E-07	1.45E-06	3.25E-04	1.45E-06
30	1.11E-06	2.49E-06	6.11E-04	2.19E-06
35	1.49E-06	4.19E-06	1.12E-03	3.25E-06
40	1.98E-06	6.93E-06	1.99E-03	4.76E-06

Calculated K_H ranged from 1.39E-7 to 1.99E-03 atm·m^3·mol^{-1} across all models and temperatures. K_H values below 3.00E-07 atm·m^3·mol^{-1} indicate the chemical is nonvolatile and likely to remain in water.[15] K_H values between 3.00E-07 to 1.00E-05 atm·m^3·mol^{-1} indicate slight volatility, while values above 1.00E-05 atm·m^3·mol^{-1} suggest substantial volatilization may occur, with rapid volatilization considered likely when exceeding 1.00E-03 atm·m^3·mol^{-1}. Van’t Hoff plots of Henry’s law constants for each model are presented in Figure 3.1.

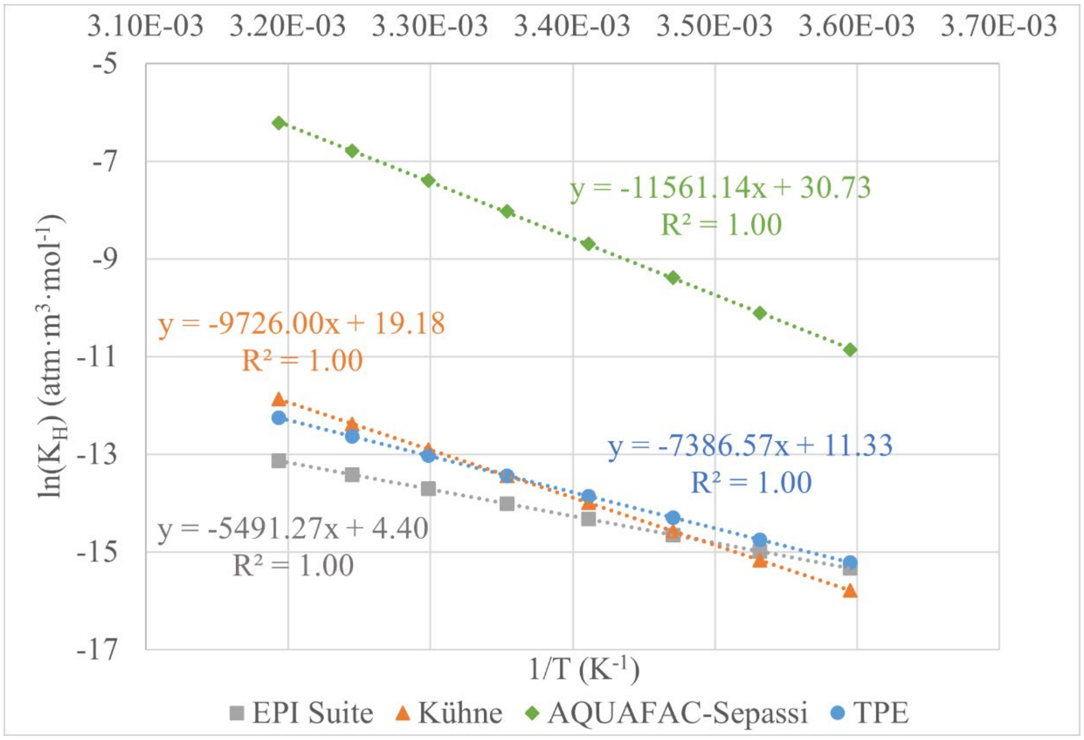

Figure 3.1 Van't Hoff plot of Henry's law constants (*K_H*) for selected models

Calculated $\Delta_{aw}H$ for EPI Suite, Kühne, AQUAFAC-Sepassi, and TPE models were 45.7, 80.9, 96.1, and 61.4 kJ·mol^{-1}, respectively. $\Delta_{aw}H$ can be described as the difference between the enthalpy of vaporization of a compound ($\Delta_{vap}H$) and its excess enthalpy in water (H_w^E) according to equation (3.10).[21]

$$\Delta_{aw}H = \Delta_{vap}H - H_w^E \tag{3.10}$$

In all cases, the excess enthalpy of vaporization was greater than the excess enthalpy of OXY in water, indicating that temperature will have a larger impact on volatility rather than the solubility of OXY.

The temperature dependence of K_H varies as a function of $\Delta_{aw}H$ [21]. For the $\Delta_{aw}H$ calculated, the expected average factor increase in K_H per 10 °C is approximately 4 for AQUAFAC-Sepassi, 3 for Kühne, and 2 for the EPI Suite and TPE models, respectively. These predictions are consistent with the increases observed in this study as presented in Table 3.2.

Table 3.2. Factor Increase in Henry's Law Constant (K_H) with Temperature for Selected Models

Temperature Increase	Factor Increase in K_H			
	EPI Suite	Kühne	AQUAFAC-Sepassi	TPE
5 to 15 °C	1.98	3.37	4.39	2.51
10 to 20 °C	1.94	3.23	4.11	2.43
15 to 25 °C	1.90	3.10	3.86	2.36
20 to 30 °C	1.85	2.99	3.64	2.30
25 to 35 °C	1.82	2.88	3.44	2.23
30 to 40 °C	1.78	2.79	3.26	2.18
5 to 40 °C	9.08	49.81	104.10	19.46
18 to 22 °C	1.29	1.57	1.71	1.41

The increase in K_H with temperature varied between the models over the full range of temperatures observed in rice fields (5 to approx. 40 °C).[9] However, rice field temperatures typically stabilize to daily fluctuations between 18 to 22 °C.[8] Within this range, there is greater agreement between the models on the magnitude of impact temperature has on K_H, with expected K_H fluctuating by a factor of roughly 1.5 across all models (Table 3.2). Under these typical field conditions, the AQUAFAC-Sepassi model indicates that OXY will be substantially volatile, while EPI Suite, Kühne, and TPE models indicate that OXY is only slightly volatile based on calculated K_H (Table 3.1).[15]

3.4.2.2 EPI Suite

K_H ranged from 2.18E-07 to 1.98E-06 atm·m^3·mol^{-1}, indicating OXY is nonvolatile to slightly volatile in rice field water. Of the four models, EPI Suite predicted relationship between K_H and temperature was weakest, as indicated by its smaller van't Hoff slope (A) and, by extension, $\Delta_{aw}H$. To determine slope A, EPI Suite uses the similar compound slope analogy method and assigned OXY the class of 'general aromatic' with a slope value of 5,500. This class was selected by the program as OXY does not contain structures corresponding to the more specific classes for which EPI Suite has data for (e.g., aniline type; aliphatic acid; aromatic acid; etc.).[20]

The K_H predicted at 20 and 25 °C for EPI Suite (5.99E-07 and 8.20E-07 atm·m^3·mol^{-1}, respectively), were in good agreement with K_H calculated from literature reported physical property data (9.52E-07 and 1.45E-06 atm·m^3·mol^{-1}, respectively). However, it was determined that EPI Suite calculates K_H at 25 °C using vapor pressure and water solubility measured at two different temperatures. The water solubility value selected by the model was 0.116 mg·L^{-1}, which represents the reported value at 25 °C.[11] However, the vapor pressure selected is 2.63E-10 atm, which is the value reported at 20 °C.[3] Mismatches such as these may stem from limitations of the PHYSPROP database from which EPI Suite extracts chemical property data, and may result from either incorrect labeling of data or the absence of a value at a particular reference temperature.[20] Although the automated nature of EPI Suite renders it convenient and user friendly, care must be exercised to ensure correct values and assumptions are employed by the model.

3.4.2.3 Kühne Model

K_H ranged from 1.39E-07 to 6.93E-06 atm·m^3·mol^{-1}, indicating OXY is nonvolatile to slightly volatile in rice field water. The $\Delta_{aw}H$ predicted by the model was closer in magnitude to the AQUAFAC-Sepassi model, while calculated K_H were in greater agreement with EPI Suite and TPE due largely to shared physical property data at the reference temperatures used by the models. The K_H calculated at 20 °C for the Kühne model was in good agreement with the literature derived value (8.33E-07 and 9.52E0-07 atm·m^3·mol^{-1}, respectively).

The Kühne model has been cross validated, with an average standard error of 7.6 kJ·mol^{-1} for $\Delta_{aw}H$, and demonstrates good predictive capability.[19] The training set compounds did not include OXY, although it was primarily composed of organic chemicals and included all OXY constituent atoms (C, H, F, Cl, N, and O). The model was also able to describe all OXY fragments, including correction factors for specific ortho-substitution and halogenated features which were discovered by Kühne, et al. to heavily influence $\Delta_{aw}H$. Given the potentially large influence of these correction factors, careful dissection and assignment of molecular structures is critical to the proper implementation of the model.[19]

3.4.2.4 AQUAFAC-Sepassi model

K_H ranged from 1.92E-05 to 1.99E-03 atm·m^3·mol^{-1}, indicating OXY is substantially volatile, with the potential to rapidly volatilize at 35 °C or higher. The AQUAFAC-Sepassi model predicted higher K_H across all temperatures, with estimated values exceeding the other models by 2 to 3 orders of magnitude above 5 °C, and exhibited the strongest relationship between temperature and volatility, as indicated by the larger $\Delta_{aw}H$. K_H estimated by the model at 20 and 25 °C were 1.68E-04 and 3.25E-04 atm·m^3·mol^{-1}, respectively. These values exceed those calculated with literature reported physical properties by a factor of over 150. One possible explanation for this discrepancy may be readily explained by comparing the vapor pressure and water solubility calculated in this approach with measured data.

Vapor pressure predicted by the AQUAFAC-Sepassi model at 20 and 25 °C were 1.01E-08 and 2.19E-08 atm, respectively, exceeding measured vapor pressures by roughly a factor of 40.[3, 11] As K_H varies directly with vapor pressure, this biases the model an equivalent degree. Water solubility predicted by the model at 20 and 25 °C were 0.022 and 0.024 mg·L^{-1}, respectively, underpredicting measured water solubilities by a factor of roughly 5.[11, 32] As K_H varies inversely with water solubility in this model, the error for both vapor pressure and water solubility are compounded in the final estimate for a total deviation factor of roughly 200 from literature-based values.

It is difficult to attribute specific causes to the discrepancies observed between the AQUAFAC-Sepassi constituent models and literature values as many parameters and assumptions are incorporated into the underlying models during their development. In calculating vapor pressure, equation (3.8) is populated by 5 chemical-specific parameters and several fixed numerical parameters.[24] The numerical parameters represent empirically fitted values developed from experimental data across multiple chemicals and for various properties, including the entropy and heat capacity of boiling and melting. This degree of complexity makes it difficult to evaluate which components, or lack thereof, may be responsible for the observed bias for OXY. However, a component known to influence vapor pressure that may not be sufficiently considered by the model is the presence and interaction of functional groups.[33] Although the model developed by Sepassi, et al. accounts to some degree for the interactions of certain functional groups via HBN, this parameter is limited in its scope to the hydrogen bonding effects of alcohols, carboxylic acids, and primary amines.[24, 34]

In contrast, a separate QSPR model was developed to predict vapor pressure based upon organic functional groups, including the full suite of contributing functional groups that constitute OXY.[33] The vapor pressure at 25 °C calculated according to this model was 4.56E-10 atm (ESI1). This prediction is in remarkably close agreement with the measured vapor pressure at the same temperature of 4.66E-10 atm. The good performance of the model may stem from the training set of compounds used to develop the model, which included many agrochemicals and was tailored specifically to predict agrochemical vapor pressure based on functional groups. This confirms that the functional groups of OXY may play an important role in its vapor pressure and volatility behavior. Despite the accuracy of the model, its ability to estimate vapor pressure is fixed at a single temperature (25 °C) rendering it unsuitable for predicting the impacts of temperature on K_H.

The parametrization scheme of AQUAFAC is simple and estimates water solubility based on the type and number of functional groups present as well as the melting point of the molecule.[25] Although solubility is a complex phenomenon, with thermodynamic and kinetic components, its key determinant is the favorability of interactions between solute and water.[35] Primarily composed of nonpolar and hydrophobic functional groups, OXY is limited in its ability to engage in favorable interactions with water molecules, leading to poor solubility. While AQUAFAC directly accounts for the contribution of these functional groups and accurately predicts the hydrophobic tendency of OXY, it underpredicts the actual degree of solubility for OXY. Factors such as molecule size, shape, and confirmational flexibility also affect solubility in water and could account for the differences in observed and predicted values.[35] Proximity effects, like steric shielding, also impact solubility and are accounted for in some cases by the AQUAFAC model; however, none of the cases apply to the structure of OXY.[36] Despite the limitations, predicted water solubilities were within an order of magnitude of measured values, which is generally regarded as an acceptable degree of accuracy when estimating fate properties.[37]

3.4.2.5 TPE Model

K_H ranged from 2.45E-07 to 4.76E-06 atm·m^3·mol^{-1}, indicating OXY is nonvolatile to slightly volatile in rice field water. The simplest of the models evaluated, TPE relies only on the availability of K_H at two distinct temperatures. Although the van't Hoff regression parameters were interpolated using only measured physical property data, the model is highly sensitive to error in the measurement of each property and inherent low sampling quantity. This creates considerable uncertainty when extrapolating K_H to other temperatures, with error increasing the further the deviation from the reference temperatures.

These limitations could be ameliorated by incorporating physical property data from additional temperatures, thereby enhancing the accuracy of interpolating $\Delta_{aw}H$, which governs K_H temperature dependence under environmentally relevant conditions.[21] However, these data were not available for OXY and are commonly limited to measurements at 25 °C, and occasionally 20 °C, for most compounds.

3.4.3 Conclusions

A simple model for evaluating the feasibility of experimental determination of K_H via GSM was developed. This model was used to establish the infeasibility of GSM for OXY, even under best-case conditions, indicating K_H is more suitably calculated for OXY rather than measured.

Four air-water partitioning models were used to calculate K_H for OXY at California rice field temperatures (5 to 40 °C). Results of EPI Suite, Kühne, and TPE models were in overall agreement, indicating OXY is predominantly slightly volatile yet potentially nonvolatile at low temperatures (5 to 10 °C). In contrast, the AQUAFAC-Sepassi model suggested volatility was substantial at all temperatures evaluated and potentially rapid above 35 °C. However, the model exhibited a lack of accuracy in predicting physical properties important in K_H estimation, suggesting limitation in its ability to capture the complex interactions and processes governing the air-water partitioning behavior of OXY. The compounding effects of these errors also highlight potential pitfalls to consider when utilizing composite QSPR models. This evaluation emphasizes the importance of model selection, comparison, and validation in accurately predicting air-water partitioning behavior for OXY and other HOCs.

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Chapter 4

Environmental Fate and Aquatic Risk Assessment of Oxyfluorfen in California Rice Fields

David J. Bonnar and Ronald S. Tjeerdema

4.1 Abstract

The herbicide oxyfluorfen [OXY; 2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl)benzene] recently emerged as a potential solution to combat herbicide resistance in California rice. Proposed as a pre-emergent applied pre-flood to soil, products are in development for use on OXY-tolerant rice strains. Currently, OXY is not registered for use with rice and its use in- or near-aquatic resources is restricted due to its high aquatic toxicity. Before OXY may be registered for use in California rice fields, its potential fate and aquatic risk must be evaluated. In this assessment, the environmental fate of OXY and its risk to aquatic organisms under simulated California rice field conditions are characterized. The Pesticides in Flooded Applications Model (PFAM) was used to estimate environmental concentrations based on anticipated use patterns and water management practices in California (e.g., winter flooding, turnover, water holding, etc.). Two California rice field soil conditions were simulated in addition to standard soil conditions used in ecological risk assessment for rice. Results suggest OXY is likely to concentrate in sediment and dissipate slowly. Water holding period had little effect on paddy and release water concentrations. Risks from water column exposure were generally below levels of concern (LOC) for aquatic animals, while risks to aquatic plants, algae, and benthic invertebrates exceeded LOCs under all conditions evaluated. California rice field soil conditions were also associated with less risk compared to standard conditions. Reduced application rates were sufficient to reduce risk to acceptable levels in some situations. However,

holding times up to 30 days had no effect on risk outcomes, suggesting water management needs of growers should be strongly considered when stipulating water holding periods for OXY.

4.2 Introduction

Herbicide resistance poses a mounting threat to rice production in California.[1-2] Thus, growers have sought to expand the selection of herbicides to ameliorate the current lack of chemical control options and leverage alternative modes of action.[3-4] One agent proposed for such purpose is oxyfluorfen (OXY, trade name Goal). OXY is a broad-spectrum, diphenyl ether herbicide that disrupts the synthesis of chlorophyll through inhibition of the protoporphyrinogen oxidase (protox) enzyme.[5] When applied as a pre-emergent to field soil, OXY has been shown effective against rice weeds, including weedy rice (*Oryza sativa f. spontanea*), a pest for which no herbicide is currently registered for in California.[3] The lack of resistance to its mode of action, in addition to the development of OXY-tolerant rice strains, has led to a surge in interest among growers, with products for use with rice already in development. However, OXY is not currently registered for use on rice and has historically been subject to prohibitions limiting its use in or near aquatic resources due to its high aquatic toxicity.[6-7]

Before an herbicide may be registered for use, it must first be evaluated for its potential to cause adverse environmental impacts by undergoing an ecological risk assessment (ERA).[8] Registered for use in a wide variety of agricultural and non-agricultural settings, OXY has been the subject of multiple ERAs, which have consistently identified risk to aquatic organisms as a chief concern.[6, 9-11]. Despite its restrictions, OXY is frequently detected in surface water and sediment.[11-13] Although concentrations rarely exceed aquatic life benchmarks, expanding its use to rice fields introduces novel opportunities for contamination and environmental impacts.

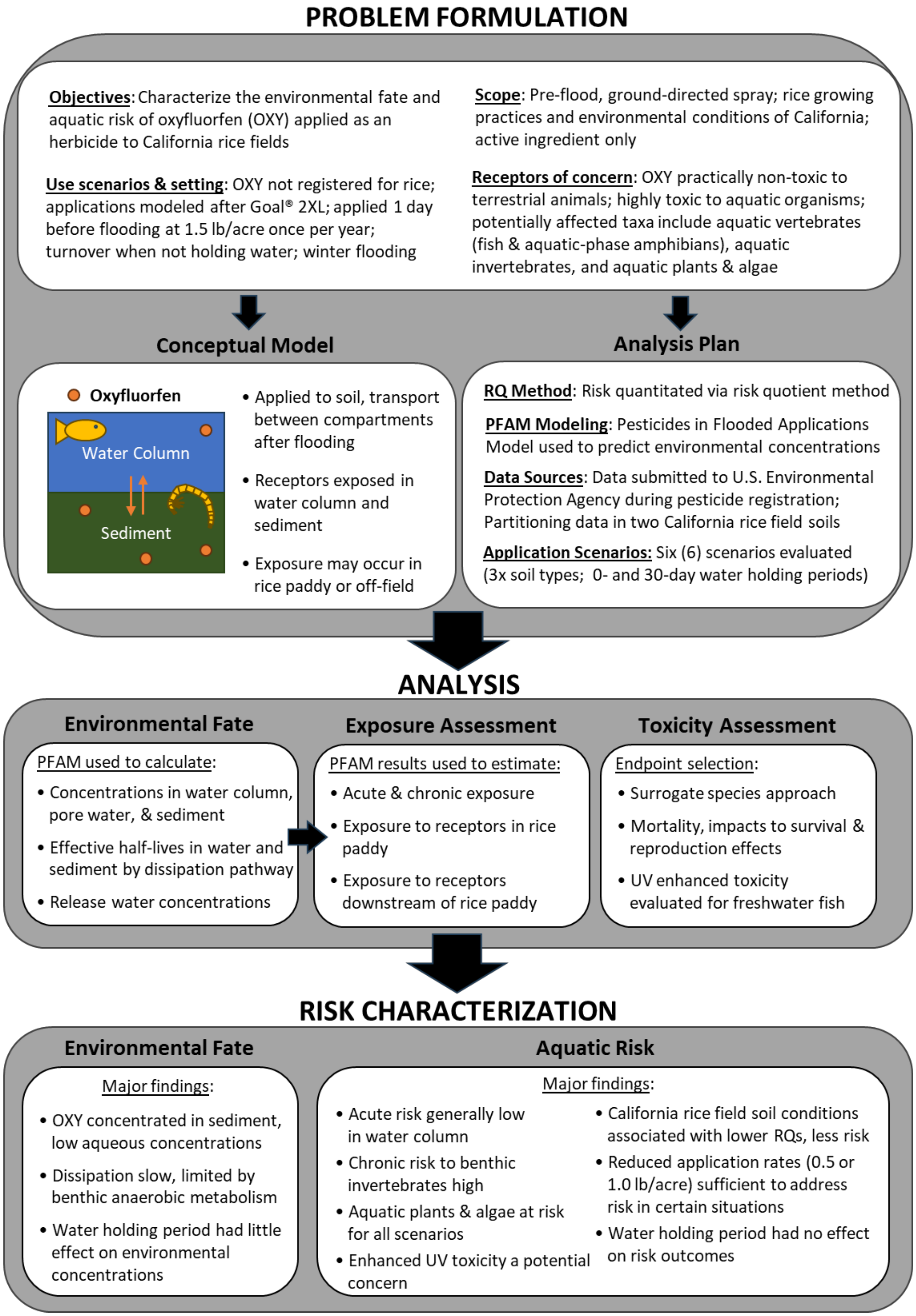
The majority of rice grown in California is produced within the Sacramento Valley.[14] California rice fields are composed of heavy clay soils which are nearly impermeable to water, restricting percolation and allowing for flooding. A unique feature of rice cultivation is the ability to conserve water by recycling into fallow fields and ultimately discharging used water into nearby waterways, such as the Sacramento River Basin. When fields are treated with herbicides, the potential exists for their discharge into receiving waters, risking exposure to sensitive aquatic life. Thus, rice pesticide labels often specify water holding periods in which water must be held on the field to allow the pesticide to dissipate. The length of this period is dependent on the overall dissipation rate of the pesticide.[15]

During water holding periods, evaporation of field water leads to progressive evapoconcentration of salts. Known for its warm, dry conditions, the Sacramento Valley is especially sensitive to this process and field salinity levels in excess of the threshold for crop yield reduction are commonly observed early in the growing season.[16] Thus, growers are vested in ensuring water is held no longer than is necessary to reduce risk to acceptable levels. This risk is directly proportional to the amount of OXY that reaches off-field water and sediment and is predicted using environmental fate models.

Models that have been used to predict the fate of OXY include the Pesticide Root Zone Model coupled with the Exposure Analysis Model System (PRZM/EXAMS) and the Pesticides in Water Calculator (PWC).[9, 11] While validated and widely used in aquatic risk assessment, these models were designed to simulate applications in non-flooded agricultural systems and are limited in their ability to account for flooded conditions or unique properties of rice fields. Furthermore, fate data used in previous assessments are not necessarily representative of rice field conditions.

A recently published study found that the affinity of OXY for California rice field soils may be greater than other soils.[17] Sorption to these soils also exhibited pronounced hysteresis, rendering OXY resistant to release into water. As soil-water partitioning processes are among the most influential and sensitive components of fate modeling, these characteristics are important to consider when predicting fate.[18-19] However, ERAs conducted with flooded agricultural models and California rice field fate data do not appear to be readily available for OXY. Thus, considerable uncertainty exists regarding the fate and impacts of OXY-based herbicides in rice fields.

In this analysis, an environmental fate and aquatic risk assessment are conducted to investigate potential environmental exposures and ecological effects associated with the use of OXY as an herbicide in California rice fields. Concentrations were calculated using the Pesticides in Flooded Applications Model (PFAM), a model developed to assess pesticide use in flooded agricultural environments and major regulatory tool in ERA for rice-based herbicides.[20] California rice field soil conditions are simulated using available data in addition to standard ERA scenarios developed by the U.S. Environmental Protection Agency (USEPA).[21] This assessment is conducted consistent with ERA guidelines[22] and its format includes three distinct sections: formulation of the problem, the analysis phase, and characterization of risk. A flowchart and summary of this assessment is provided in Figure 4.1.



PROBLEM FORMULATION

Objectives: Characterize the environmental fate and aquatic risk of oxyfluorfen (OXY) applied as an herbicide to California rice fields

Scope: Pre-flood, ground-directed spray; rice growing practices and environmental conditions of California; active ingredient only

Use scenarios & setting: OXY not registered for rice; applications modeled after Goal® 2XL; applied 1 day before flooding at 1.5 lb/acre once per year; turnover when not holding water; winter flooding

Receptors of concern: OXY practically non-toxic to terrestrial animals; highly toxic to aquatic organisms; potentially affected taxa include aquatic vertebrates (fish & aquatic-phase amphibians), aquatic invertebrates, and aquatic plants & algae

Conceptual Model

- Applied to soil, transport between compartments after flooding
- Receptors exposed in water column and sediment
- Exposure may occur in rice paddy or off-field

Analysis Plan

RQ Method: Risk quantitated via risk quotient method

PFAM Modeling: Pesticides in Flooded Applications Model used to predict environmental concentrations

Data Sources: Data submitted to U.S. Environmental Protection Agency during pesticide registration; Partitioning data in two California rice field soils

Application Scenarios: Six (6) scenarios evaluated (3x soil types; 0- and 30-day water holding periods)

ANALYSIS

Environmental Fate

PFAM used to calculate:

- Concentrations in water column, pore water, & sediment
- Effective half-lives in water and sediment by dissipation pathway
- Release water concentrations

Exposure Assessment

PFAM results used to estimate:

- Acute & chronic exposure
- Exposure to receptors in rice paddy
- Exposure to receptors downstream of rice paddy

Toxicity Assessment

Endpoint selection:

- Surrogate species approach
- Mortality, impacts to survival & reproduction effects
- UV enhanced toxicity evaluated for freshwater fish

RISK CHARACTERIZATION

Environmental Fate

Major findings:

- OXY concentrated in sediment, low aqueous concentrations
- Dissipation slow, limited by benthic anaerobic metabolism
- Water holding period had little effect on environmental concentrations

Aquatic Risk

Major findings:

- Acute risk generally low in water column
- Chronic risk to benthic invertebrates high
- Aquatic plants & algae at risk for all scenarios
- Enhanced UV toxicity a potential concern
- California rice field soil conditions associated with lower RQs, less risk
- Reduced application rates (0.5 or 1.0 lb/acre) sufficient to address risk in certain situations
- Water holding period had no effect on risk outcomes

Figure 4.1. Structure and summary outline of the environmental fate and aquatic risk assessment conducted

4.3 Problem Formulation

The first step in ERA is problem formulation.[22] Its purpose is to provide the foundation for the assessment through establishing its objectives, scope, and strategies for data analysis. At its conclusion, a conceptual model and analysis plan are developed.

4.3.1 Objectives

The objective was to evaluate the environmental fate of OXY applied as an herbicide to California rice fields and determine the potential for harm to aquatic organisms resulting from its use. Fate characteristics of interest include environmental concentrations, the relative contribution of dissipation pathways, and the effects of water holding period on release water concentration. Adverse effects of interest include mortality and negative impacts to reproduction or survival.

4.3.2 Scope of Analysis

This assessment considers environmental transport, dissipation, and potential exposure and risk to aquatic species resulting from pre-flood, ground-directed applications of OXY to California rice field soils. The focus is on rice growing practices and environmental conditions typical to California. Contamination and risk associated with accidental misuse (e.g., spills, misapplication, overapplication), aerial applications, or direct applications to water are not considered. This assessment is limited to the active ingredient OXY and does not include inert ingredients or degradates. Species federally listed as a threatened or endangered are not evaluated separately.

4.3.3 Use Scenarios & Setting

Use scenarios provide a description of how a chemical substance is used, released, or otherwise introduced into the environment. The setting describes the environment and context in which the substance is used. Both are used in preparation of a conceptual model and development of application scenarios for analysis. As OXY is not currently registered for use in rice fields, the use scenarios described below are hypothetical and based on typical use patterns for OXY-based products, practices regularly employed by rice growers in California, and on current herbicide development programs for OXY-tolerant rice strains (K. Al-Khatib, personal communication, October 16, 2023)

Application of OXY-based products to California rice fields were modeled after use patterns of Goal® 2XL (Nufarm, Melbourne, Australia), as described by Galvin, et al. [3], with an anticipated application rate of 1.5 lb/acre in rice fields (K. Al-Khatib, personal communication, October 16, 2023). OXY is applied as a liquid formulation pre-flood to rice field soil. Fields are then flooded 1 day after application and maintained at 4 inches depth for the growing season. Flooding and planting typically occur between the beginning of April to the end of May.[14]

During the growing season, rice growers in California commonly maintain water turnover at a low rate to prevent algae growth, resulting in the continual, low-level release of water from the flooded field (paddy) to canals and downstream water bodies. However, turnover is restricted during label-specified water holding periods, which typically span between 7 and 30 days depending on the degradation rate of the pesticide.[15] Fields usually remain flooded until 2 weeks from harvest, at which point the field is drained, typically between mid-September to mid-October.

After harvest, fields are flooded to aid straw decomposition and nutrient recycling. Flood levels are typically maintained for the winter, usually between October to February. During this period, the fields serve as important wildlife habitat.[14] After winter flooding, the fields are drained, and land is prepared for a new season of growing.

OXY may be applied once per year prior to flooding at the beginning of each growing season. At any point in the annual cycle, OXY has the potential be transported off-site to canals or waters downstream of treated fields via runoff and erosion when water is released from the field. These releases may be intentional (e.g., water turnover; scheduled draining; etc.) or unintentional (e.g., overflow from field following precipitation). OXY residues may move from soil into the water column, or vice versa, throughout environmental transport.

4.3.4 Receptors of Concern

Exposure of non-target organisms (receptors) to OXY may occur in the paddy, canals or receiving waterbodies (freshwater and saltwater). In the Sacramento Valley, such waterbodies host fish, amphibians, aquatic and sediment dwelling (benthic) invertebrates, plants, and algae.[14, 23] Although OXY is practically non-toxic to terrestrial organisms (e.g., mammals, birds, honeybees, etc.), it is highly toxic to fish and very highly toxic to invertebrates (aquatic and benthic) according to USEPA toxicity categories.[11] It is also harmful to plant and algae growth.

Receptors of concern are identified for assessment of risk based on the simultaneous consideration of potential exposure and sensitivity to OXY. Receptors are divided into broad taxonomic groups based on the primary source of exposure to contaminated media (water column or benthic sediment). Groups include aquatic vertebrates, aquatic invertebrates, and benthic invertebrates, and are further subdivided into freshwater and saltwater types. In this assessment, fish serve as surrogates to vertebrates, specifically aquatic-phase amphibians. Aquatic plants form another group and are subdivided into vascular and non-vascular types. For purposes of this analysis, algae are included in the aquatic plants (non-vascular) group.

4.3.5 Conceptual Model

For OXY to pose aquatic risk, it must reach receptors in biologically relevant concentrations. This requires that a feasible route of exposure, referred to as an exposure pathway, be complete. To be complete, it must have a 1) source, 2) release mechanism, 3) medium of transport, and 4) point of exposure for an aquatic receptor.[22] A conceptual model is a visual representation of these pathways and is used to identify relevant environmental media and receptors to consider in ERA. A model for the soil-directed application of OXY to California rice field soil is illustrated in Figure 4.2.

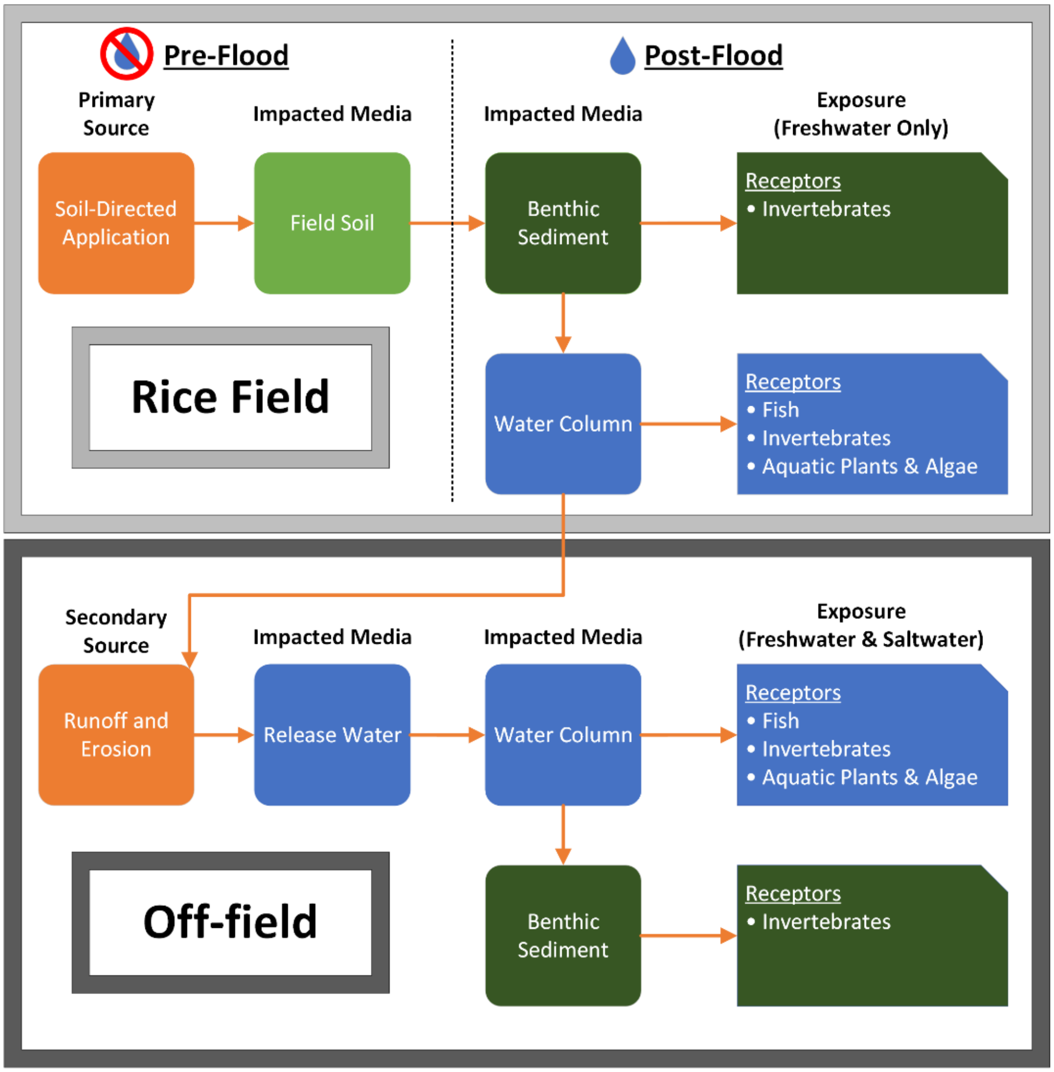


Figure 4.2. Conceptual model for pre-flood, soil-directed pesticide application to rice field soil and complete exposure pathways after flooding. Orange arrows indicate transport of pesticide through environmental media to aquatic receptors. Off-field sites include canals and water bodies downstream of the rice field.

After initial application to rice field soil and subsequent field flooding, OXY is released from sediment into the water column. Runoff and erosion allow for off-site transport, resulting in contamination of off-field water and sediment in both freshwater and saltwater environments. Exposure of aquatic receptors to OXY occur through these contaminated media. Fish, water column invertebrates, and aquatic plants are exposed through water, while benthic invertebrates are exposed through sediment.

4.3.6 Analysis Plan

4.3.6.1 RQ Method

Risk to aquatic receptors is characterized through the risk quotient (RQ) method.[8] RQs are calculated by dividing estimated environmental concentrations (EECs) by toxicity endpoints (TEs) according to equation (1):

$$RQ = \frac{EEC}{TE} \tag{1}$$

EECs were calculated via the Pesticides in Flooded Applications Model (PFAM), described below. TEs are measures of toxicity that indicate the threshold of exposure that produces a toxic effect in a species. Common TEs include the median lethal concentration (LC50), median effective concentration (EC50), and no observable adverse effect level (NOAEL). Calculated RQ are compared to levels of concern (LOCs) to characterize the potential for adverse effects. The LOCs are set based on receptor group and whether the exposure is short-term (acute) or long-term (chronic). For acute and chronic risks to aquatic animals, the LOC are 0.5 and 1.0, respectively. For risks to aquatic plants, the LOC is 1.0. When a calculated RQ exceeds the LOC, the organism is considered at risk for adverse effects.

This assessment uses the surrogate species approach.[8] As such, toxicological data from surrogate test species are used to represent the broad taxonomic groups identified by the receptors of concern in this analysis. These toxicological data form the TE used to calculate RQs. For characterizing risk to aquatic animals, the lowest median lethal concentration (LC50) is used to characterize acute risk, while the lowest No Observable Adverse Effect Concentration (NOAEC) is used to characterize chronic risk. For aquatic plants, the lowest EC50 is used to characterize risk. In the absence of TE data for a particular taxonomic group, TE for the most similar group for which data are available may be used. As fish serve as surrogates to vertebrates, conclusions of risk apply equally to aquatic-phase amphibians.

The toxicity of OXY has been found to be enhanced in the presence of ultraviolet (UV) light in chronic exposure studies with freshwater fish.[11] In the environment, fish may be exposed concomitantly to UV and OXY while swimming water that is sufficiently shallow and clear. Thus, an additional exposure category, referred to as UV Chronic, was characterized to evaluate the risk to freshwater fish resulting from chronic exposure to OXY under UV enhanced conditions.

4.3.6.2 PFAM modeling

The concentration of OXY in the paddy water column, release water, benthic sediment, and benthic pore water following pre-flood application to field soil was estimated using the Pesticides in Flooded Applications Model (PFAM) Version 2.[20] PFAM is a water model developed by the USEPA to estimate pesticide concentrations in surface water and sediment following applications in flooded agricultural systems, such as rice fields and cranberry bogs. It simulates pesticide partitioning, dissipation, and degradation processes through consideration of its physical and chemical properties, the properties of the environment, and agricultural management practices. Concentrations are reported in a manner readily used by the USEPA in aquatic risk assessments (e.g., 1-in-10-year events for 1-day, 21-day, and 60-day averages). PFAM is validated, non-proprietary, and freely available to the public for both inspection and use.[24]

4.3.6.3 Data sources

Physical-chemical property and toxicity data used in the assessment were primarily derived from studies submitted to and reviewed by the USEPA during registration processes for OXY.[6, 9-11] These studies must meet guideline criteria set by the USEPA to ensure study quality and sufficient applicability for ERA within the broad range of environments in which OXY is registered for use.

Currently OXY is not registered for use in rice fields; as a result, fate data for California rice fields is limited within the open literature. However, a study was recently published characterizing the soil-water partitioning of OXY in two California rice field soils collected from two separate fields near Davis, CA (Davis soil) and in Biggs, CA (Biggs soil).[17] Data from this study, including the organic carbon-water partition coefficient (K_{oc}) and fraction organic carbon (f_{oc}) for each soil, were included to simulate site-specific partitioning conditions.

4.3.6.4 Application scenarios

Application scenarios describe the manner and environmental conditions in which a pesticide may be used.[22] They are used to select input parameters for PFAM simulations and define individual runs of the model. As a label specified holding period for OXY is not yet available, water holding periods of 0 days (none) and 30 days were simulated to generate lower- and upper-bound EECs for paddy and release water concentrations and to evaluate the impacts of holding period. The default characteristics for the standard rice field developed by the USEPA for use in ERA, including soil characteristics (standard soil), were selected for simulation.[20] Applications to Davis and Biggs soils (site-specific soils) were also simulated.[17] In total, six (6) distinct application scenarios were constructed to calculate EECs using PFAM and are presented in Table 4.1. Each scenario was assigned a unique Scenario ID and carried through to risk characterization.

Table 4.1 Application Scenarios Selected for PFAM Simulation of OXY Applications to California Rice Fields[a]

Scenario ID	Application Environment	Water Holding Period (days)
S-00	Standard Soil (f_{oc}: 1.0%)[b]	0
S-30		30
D-00	Davis Soil (f_{oc}: 2.41%)[c]	0
D-30		30
B-00	Biggs Soil (f_{oc}: 1.61%)[c]	0
B-30		30

[a]Abbreviations: Pesticides in Flooded Applications Model (PFAM), oxyfluorfen (OXY), fraction organic carbon (f_{oc})
[b]Standard soil characteristics as described by Young.[20]
[c]Site-specific soil characteristics as described by Bonnar et al.[17]

4.3.6.5 Parametrization

To simulate fate in rice fields, PFAM requires 5 major categories of input: 1) the physical-chemical properties of the pesticide, 2) the method and date of application, 3) flooding conditions and schedule, 4) rice crop phenology, and 5) climate, soil, and water characteristics within the region. Table 4.2 below summarizes the physical-chemical properties of OXY used in PFAM simulation. For all scenarios, one application per year on May 2 at an application rate of 1.5 lb/acre (1.68 kg/ha) was simulated. The standard PFAM scenario file for ERA in rice fields of California (ECO CA Winter.PFS) was selected for all scenarios.[21] PFAM scenario files are developed by the USEPA and populate the floods, crop, and physical tabs of PFAM with default values (e.g., standard soil) that are generally representative of the environmental conditions and flood management practices within a specified region. Turnover was set to 0 day^{-1} for the water holding period (0 or 30 days), then returned to the default value (0.017 day^{-1}; 1 in 60 days) until harvest and during winter flooding. For scenarios simulating Davis and Biggs soils, the fraction organic carbon (f_{oc}) associated with benthic sediment was set to 0.0241 and 0.0161, respectively, while the average K_{oc} measured in each soil was used.[17] Heat of Henry (J/mol) was calculated via

EPI Suite v4.11 according to the guidance provided in the PFAM User Guide.[24-25] Full input parameters for each scenario are available in the Electronic Supporting Information 2 (ESI2; https://doi.org/10.6084/m9.figshare.24584949).

Table 4.2. Physical-chemical Properties of OXY Used in PFAM Simulation[a]

Parameter	Value	Superscript Citation
K_{oc} (mL/g)	Standard: 12233	11
	Davis Soil: 73586	17
	Biggs Soil: 97656	17
Water Column Half-life at 20 ℃ (d)	34	11
Benthic Metabolism Half-life at 20 ℃ (d)	425	11
Unflooded Soil Half-life at 20 ℃ (d)	680	11
Near-Surface Photolysis Half-life at 40° Latitude (d)	7.56	11
Hydrolysis Half-life (d)	1.00E+08	11
Molecular Weight (g/mol)	361.7	11
Vapor Pressure at 25 ℃ (Torr)	3.5E-07	11
Solubility in Water at 25 ℃ (mg/L)	0.116	11
Heat of Henry at 25 ℃ (J/mol)	45727	25

[a]Abbreviations: oxyfluorfen (OXY), Pesticides in Flooded Applications Model (PFAM)

4.4 Analysis

4.4.1 Environmental Fate

4.4.1.1 Estimated environmental concentrations

PFAM was used to calculate 1-in-10 year EECs in the water column, benthic pore water, and benthic sediment. These EECs are calculated as peak, 1-day, 4-day, 21-day, 60-day, 90-day, and 365-day averages. EECs used in calculation of RQs are described in the Exposure Assessment section.

4.4.1.2 Dissipation pathways

During each simulation, PFAM calculates the effective half-life for each dissipation pathway (available as *Output*_paddy_AncillaryInfo.txt) within water column and sediment compartments. They account for factors that that affect dissipation (e.g., shading from plants, temperature, water level and flow, etc.) and are averaged over the simulation duration (D. Young, personal communication, August 15, 2023). Represented as first-order processes, they include water column microbial metabolism, hydrolysis, photolysis, volatilization, and washout (transport of pesticide off-field via water flow) for the water column compartment, and benthic anaerobic metabolism and hydrolysis for the sediment compartment. As both aqueous and sorbed phases of pesticides are considered at equilibrium within a given compartment, changes in pesticide concentration in one phase dictate the concentration of other phases and allow for the calculation of an overall dissipation rate (cumulative half-life). [24] Thus, the cumulative half-life and percent contribution of each dissipation pathway to the total dissipation were calculated in both water column and sediment compartments.

4.4.1.3 Release water concentrations

The Water Holding Calculator tool available in PFAM Version 2 was used to calculate the release water concentration (90th percentile) immediately after flooding and each day incrementally for 30 days for each scenario. These values were used to evaluate the impacts of water holding period on release water concentrations and risk to receptors downstream from the paddy. Note that turnover (loss of water from field) is maintained throughout the simulation for 0-day (no hold) scenarios.

4.4.2 Exposure Assessment

In ERA, exposure to aquatic organisms is evaluated using paddy concentrations.[14] Acute and chronic exposure levels for calculation of RQs were selected for each receptor group based on exposure pathway and daily average EECs, consistent with USEPA guidance.[8, 11] For acute and chronic risks to fish, the water column 1-day and 60-day averages were used, respectively.

For acute and chronic risk to aquatic invertebrates, water column 1-day and 21-day averages were used. For acute and chronic risk to benthic invertebrates from pore water exposure, benthic pore water 1-day and 21-day averages were used. For chronic risk to benthic invertebrates from bulk sediment exposure, the benthic sediment 21-day average was used. Bulk sediment concentrations used to calculate RQs were normalized to organic carbon content by dividing by the fraction organic carbon reported by the study. For risk to aquatic plants and algae, the water column 1-day average was used.

A separate exposure assessment for receptors downstream of the paddy (off-field) was also conducted using release water concentrations. This was done to evaluate the impacts of water holding period to aquatic risk off-field. Acute water column exposure was evaluated using release water concentrations calculated on the day of flooding and each day after flooding for 30 days. This approach represents an upper limit estimate of exposure as concentrations in adjacent waterbodies are expected to be lower than those in the paddy.[14]

4.4.3 Toxicity Assessment

Toxicity endpoints were obtained from the USEPA draft ERA for OXY[11], which presents the most recent and complete toxicity data set available at the time of the assessment. These endpoints reflect the threshold of exposure at which exceedance introduces the potential for mortality or impacts to survival or reproduction for the receptor group. The values used to calculate RQ are presented in Table 4.3.

Table 4.3. Toxicity Endpoints Selected for Risk Quotient Calculations for OXY by Receptor Group[a,b]

Exposure Category	Exposure Source	Test Species	Toxicity Endpoint		
			Type	Value	Unit
Freshwater Fish (surrogates for vertebrates)					
Acute	Water Column	Bluegill sunfish (*Lepomis macrochirus*)	LC50	200	µg/L
Chronic	Water Column	Fathead minnow (*Pimephales promelas*)	NOAEC	38	µg/L
UV Chronic[c]	Water Column	Fathead minnow (*Pimephales promelas*)	NOAEC	1.3	µg/L
Saltwater Fish (surrogates for vertebrates)					
Acute	Water Column	Sheepshead minnow (*Cyprinodon variegatus*)	LC50	11[d]	µg/L
Chronic	Water Column	Sheepshead minnow (*Cyprinodon variegatus*)	NOAEC	4.09	µg/L
Freshwater Invertebrates					
Acute	Water Column	Waterflea (*Daphnia magna*)	LC50	1500	µg/L
Chronic	Water Column	Waterflea (*Daphnia magna*)	NOAEC	13	µg/L
Saltwater Invertebrates					
Acute	Water Column	Grass shrimp (*Palaemonetes pugi*)	LC50	31.7	µg/L
Chronic	Water Column	Mysid shrimp (Mysidopsis bahia)	NOAEC	8.1	µg/L
Freshwater Invertebrates (benthic)					
Sub-chronic	Bulk Sediment	Midge (*Chironomus tentans*)	NOAEC	2750[e]	µg/kg-oc
Sub-chronic	Pore Water	Midge (*Chironomus tentans*)	NOAEC	484.5	µg/L
Saltwater Invertebrates (benthic)					
Chronic	Bulk Sediment	Marine Amphipod (*Leptocheirus plumulosus*)	NOAEC	400[e]	µg/kg-oc
Chronic	Pore Water	Marine Amphipod (*Leptocheirus plumulosus*)	NOAEC	27.9	µg/L
Aquatic Plants and Algae					
Vascular	Water Column	Duckweed (*Lemna gibba*)	EC50	0.33	µg/L
Non-vascular	Water Column	Marine diatom (*Skeletonema costatum*)	EC50	1.1	µg/L

[a] Abbreviations: oxyfluorfen (OXY), median-lethal concentration (LC50), no observable adverse effect concentration (NOAEC), median effective concentration (EC50)

[b] Toxicity endpoint data obtained from USEPA (2019) draft ecological risk assessment for OXY.[11]

[c] Study conducted under UV lighting conditions.

[d] Non-definitive endpoint (>11 µg/L). No mortality or sublethal effects observed in study.

[e] Bulk sediment concentration normalized to organic carbon content by dividing by the fraction organic carbon reported by the study.

Due to the lack of endpoints available, acute risk to benthic freshwater invertebrates from pore water exposure was assessed using the acute toxicity endpoint (LC50) for water column exposure to freshwater invertebrates (1500 µg/L). Similarly, acute risk to benthic saltwater invertebrates from pore water exposure was assessed using the acute toxicity endpoint (LC50) for water column exposure to saltwater invertebrates (31.7 µg/L).

Although currently available data for the enhanced toxicity of OXY under UV conditions is only available for freshwater fish, OXY is potentially more toxic under UV conditions to all receptor groups.[11] Comparison of the chronic and UV chronic endpoints for freshwater fish indicates that the toxicity of OXY is enhanced by roughly a factor of 30x under UV conditions. However, it is uncertain what the degree of enhancement would be for other species, if any, and guidance for surrogate selection for other receptors is not currently available. Thus, the risk of chronic exposure under UV conditions is addressed qualitatively during the risk characterization for other receptors.

4.5 Risk Characterization

The final phase is risk characterization, where environmental fate, exposure, and toxicity data are integrated to evaluate the potential for risk. Uncertainties, strengths, and limitations of the analysis are discussed, and conclusions are drawn. All data utilized or produced in this assessment, including PFAM input files, results, and metadata for all scenarios are available in the ESI2.

4.5.1 Environmental Fate

4.5.1.1 Estimated Environmental Concentrations

Calculated paddy EECs used in RQ calculation are presented in Table 4.4, while all other EECs are available in the ESI2. OXY predominantly partitioned into benthic sediment, with concentrations exceeding those in the water column by roughly two orders of magnitude for standard soil scenarios and three orders of magnitude for site-specific soil scenarios. Water column and pore water concentrations were roughly an order of magnitude greater in the standard soil scenarios, consistent with the lower K_{oc} and f_{oc} associated with the soil. Although bulk sediment concentrations (µg/kg) were greater for Davis and Biggs soil scenarios (ESI2), the organic carbon-normalized sediment concentrations (µg/kg-oc) were lower than those in standard soil. As exposure is evaluated using organic-carbon normalized concentrations, OXY sorbed to Davis or Biggs sediment is effectively less bioavailable for purposes of RQ calculation.

Table 4.4. PFAM Calculated 1-in-10 Year Paddy EECs Used in RQ Calculation[a]

Scenario ID	1-in-10 Year EEC					
	Water Column			Benthic Pore Water		Benthic Sediment[b]
	1-day Avg	21-day Avg	60-day Avg	1-day Avg	21-day Avg	21-day Avg
	µg/L	µg/L	µg/L	µg/L	µg/L	µg/kg-oc
S-00	31.7	30.8	29.3	34.4	33.3	408,000
S-30	32.2	31.4	29.8	34.5	33.5	411,000
D-00	3.01	2.97	2.89	3.04	3.00	220,747
D-30	3.02	2.98	2.90	3.04	3.00	220,747
B-00	3.34	3.30	3.20	3.37	3.32	324,845
B-30	3.34	3.30	3.21	3.37	3.33	324,845

[a] Abbreviations: Pesticides in Flooded Applications Model (PFAM), estimated environmental concentration (EEC), risk quotient (RQ)

[b] Organic-carbon normalized sediment concentration (µg/kg-oc) were obtained by dividing the bulk sediment concentration by the benthic f_{oc} simulated in the scenario.

Water column and pore water concentrations remained relatively steady, decreasing by roughly 4-7% in the water column between 1- and 60-day averages, and 1-3% in pore water between the 1-day and 21-day averages. Water column, pore water, and sediment EECs used in RQ calculation were insensitive to water holding period, with percent differences between 0-day and 30-day water holding period simulations ranging between 0% to 1.93% across all scenarios.

However, EECs were lower for 0-day (no hold) water holding scenarios which included turnover throughout the simulation, enhancing the dissipation of OXY in the rice field. Overall, these results indicate that OXY will be persistent in all compartments, yet predominantly concentrated in sediments.

4.5.1.2 Dissipation Pathways

Effective compartment half-lives for water column dissipation pathways are presented in Table 4.5. As OXY does not hydrolyze, the cumulative compartment half-life in the sediment is equivalent to the effective anaerobic metabolism half-life, which was 610.6 days for all scenarios. OXY dissipated much faster in the water column, with cumulative half-lives ranging from 9.4 to 10.5 days. Dissipation of OXY in the water column was primarily driven by non-degradative processes, which contributed to more than 70% of total dissipation within the water column for all scenarios, with roughly equal contribution from volatilization and washout. Overall, water holding period had only a small impact on dissipation. Water column cumulative half-lives were slightly longer in 30-day water holding scenarios, with the contribution of washout being slightly reduced as no turnover is simulated during the holding period.

Table 4.5. Water Column Effective Half-Lives by Dissipation Pathway[a]

Dissipation Pathway[b]	Effective Half-Life (days) (% Contribution to Total Dissipation)					
	S-00	**S-30**	**D-00**	**D-30**	**B-00**	**B-30**
Aerobic Metabolism	62.0 (15.1%)	62.0 (15.6%)	62.0 (16.0%)	62.0 (16.6%)	62.0 (16.4%)	62.0 (16.9%)
Photolysis	83.3 (11.2%)	83.3 (11.6%)	94.5 (10.5%)	94.5 (10.9%)	98.9 (10.2%)	98.9 (10.6%)
Volatilization	25.0 (37.4%)	25.0 (38.6%)	28.4 (34.9%)	28.4 (36.2%)	29.7 (34.1%)	29.7 (35.3%)
Washout	25.8 (36.3%)	28.3 (34.2%)	25.8 (38.5%)	28.3 (36.4%)	25.8 (39.3%)	28.3 (37.1%)
Cumulative	**9.4**	**9.7**	**9.9**	**10.3**	**10.1**	**10.5**

[a] Abbreviations: Pesticides in Flooded Applications Model (PFAM), oxyfluorfen (OXY)
[b] OXY does not hydrolyze, thus leakage from the water column through the benthic region is not simulated by default in standard PFAM scenarios for ecological risk assessment.[6, 21]

As OXY is predicted to be primarily concentrated in the sediment (Table 4.4), overall dissipation rates in rice fields depend heavily on anaerobic metabolism. With an effective sediment half-life of nearly 2 years, OXY can be expected to dissipate slowly and sediment concentrations may increase over time until total mass dissipated per year across all pathways equals the annual application rate. According to raw daily output data produced during PFAM simulations (*Output*_paddy_DailyRecord.txt), average yearly benthic total concentrations accumulated until the 6th application cycle for all scenarios, after which concentrations became more stable.

4.5.1.3 Release Water Concentrations

Calculated daily release water concentrations ranged from 2.82 to 31.32 µg/L across all scenarios (Figure 4.3). Overall, release water concentrations decreased slowly over time. The influence of water holding period was minor, with concentrations remaining relatively stable up to 30 days of holding for all scenarios. Release water concentrations for standard soil scenarios were the highest and most impacted by holding time, averaging roughly 30 µg/L over the simulation period and with a 7% and 8% drop from initial levels after 30 days of water holding for scenarios S-00 and S-30, respectively. In contrast, site-specific scenarios were largely insensitive to holding period, maintaining an average release water concentration of approximately 3 µg/L throughout the simulation and only a 4% drop from initial levels after 30 days of water holding for both no hold and 30-day holding scenarios. The increased sensitivity of standard soil scenarios to holding time is largely explained by higher EECs in the water column compartment (Table 4.4), where dissipation occurs at a faster rate (Table 4.5).

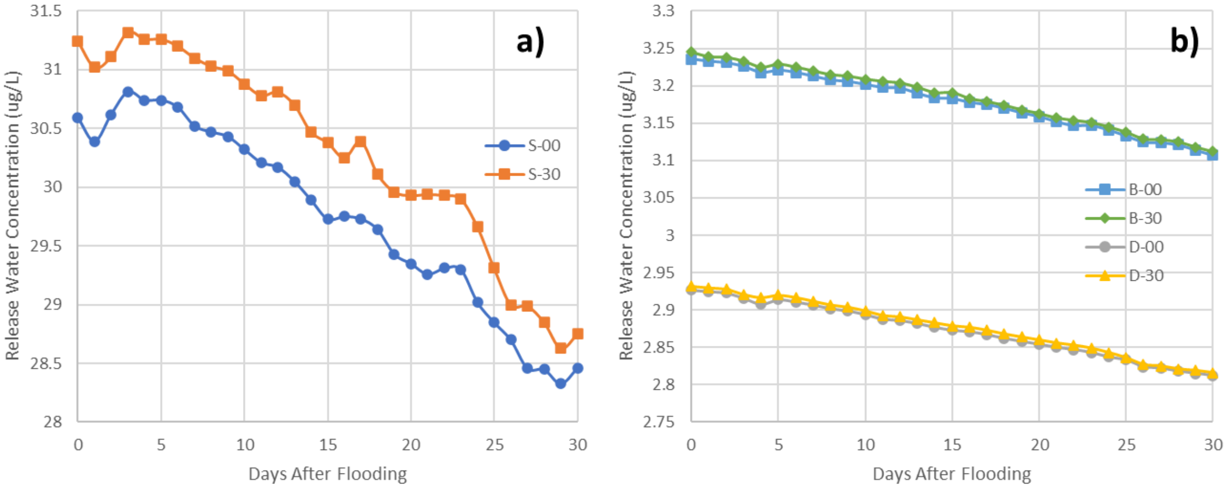


Figure 4.3. Daily release water concentrations after field flooding for a) standard soil scenarios and b) Biggs and Davis (site-specific) soil scenarios

Although release water concentrations were expectedly lower for scenarios simulating constant turnover (0 day holding), differences were minimal compared to scenarios without turnover (30-day holding). The difference between daily release water concentrations for 0- and 30-day hold scenarios did not exceed 2.3%, 0.31%, and 0.28% for standard, Davis, and Biggs soil scenarios, respectively. These results indicate that dissipation from the field is slow and largely uninfluenced by water holding period under all conditions evaluated.

4.5.2 Aquatic Risk

Calculated RQs for aquatic receptors exposed to OXY in the paddy are presented in Table 4.6 while RQs for acute exposure of downstream receptors to release water are presented in the ESI2. Where an RQ exceeds the LOC, the receptor is considered at risk for adverse effects, including mortality and negative impacts to reproduction or survival. As EECs and RQs are directly proportional to the application rate simulated, the effects of reduced application rates can be determined. Thus, application rates of 0.5 and 1.0 lb/acre were selected based on rice weed efficacy studies and evaluated for their potential to address risk concerns.[3]

Overall, risk from acute exposure to OXY in the water column was generally low (RQ < 0.1) for aquatic animals and did not exceed the LOC, except for saltwater fish and invertebrates exposed under standard soil conditions. Risk to benthic organisms from chronic exposure to OXY in the sediment was high ($RQ \geq 80.3$), exceeding the LOC for all scenarios. RQs and the frequency of LOC exceedances were higher in scenarios simulating standard soil conditions. Risk conclusions for site-specific scenarios were identical, although RQs for Biggs soil scenarios were generally higher than those for Davis soil. Water column acute and chronic (except UV chronic) RQs for site-specific scenarios were also below LOCs for all aquatic animals. Although RQs for 30-day holding period scenarios were equal to or higher than their no hold (0-day) counterparts, conclusions of risk were unaffected. While RQs for acute exposure to release water generally decreased the longer water was held, no change in risk outcome was observed for any receptor or scenario with longer (up to 30 days) holding periods. Risks to each receptor group are discussed below.

Table 4.6. Acute and Chronic RQs for Aquatic Receptors Exposed to OXY in the Paddy[a]

Exposure		LOC	Risk Quotient (RQ)[b,c]					
Category	**Duration**		**S-00**	**S-30**	**D-00**	**D-30**	**B-00**	**B-30**
Freshwater Fish (surrogates for vertebrates)								
Water Column	Acute	0.5	0.2	0.2	<0.1	<0.1	<0.1	<0.1
Water Column	Chronic	1.0	0.8	0.8	<0.1	<0.1	<0.1	<0.1
Water Column	UV Chronic	1.0	**22.5**	**22.9**	**2.2**	**2.2**	**2.5**	**2.5**
Saltwater Fish (surrogates for vertebrates)								
Water Column	Acute	0.5	**2.9**	**2.9**	0.3	0.3	0.3	0.3
Water Column	Chronic	1.0	**7.2**	**7.3**	0.7	0.7	0.8	0.8
Freshwater Invertebrates								
Water Column	Acute	0.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Water Column	Chronic	1.0	**2.4**	**2.4**	0.2	0.2	0.3	0.3
Saltwater Invertebrates								
Water Column	Acute	0.5	**1.0**	**1.0**	<0.1	<0.1	0.1	0.1
Water Column	Chronic	1.0	**3.8**	**3.9**	0.4	0.4	0.4	0.4
Freshwater Invertebrates (benthic)								
Pore Water	Acute	0.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pore Water	Sub-Chronic	1.0	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sediment	Sub-Chronic	1.0	**148.4**	**149.5**	**80.3**	**80.3**	**118.1**	**118.1**
Saltwater Invertebrates (benthic)								
Pore Water	Acute	0.5	**1.1**	**1.1**	<0.1	<0.1	0.1	0.1
Pore Water	Chronic	1.0	**1.2**	**1.2**	0.1	0.1	0.1	0.1
Sediment	Chronic	1.0	**1020.0**	**1027.5**	**551.9**	**551.9**	**812.1**	**812.1**
Aquatic Plants (vascular)								
Water Column	NA	1.0	**96.1**	**97.6**	**9.1**	**9.2**	**10.1**	**10.1**
Aquatic Plants (non-vascular)								
Water Column	NA	1.0	**28.8**	**29.3**	**2.7**	**2.7**	**3.0**	**3.0**

[a] Abbreviations: risk quotient (RQ), oxyfluorfen (OXY), level of concern (LOC), ultraviolet (UV)
[b] Bold values indicate the RQ is above the LOC.
[c] Highlighting color indicates the following: Yellow = RQ is below the LOC when application rate is reduced to 1 lb/acre; Orange = RQ is below LOC when application rate is reduced to 0.5 lb/acre; Red = An application rate lower than 0.5 lb/acre required to reduce RQ below LOC.

4.5.2.1 Fish (surrogates for vertebrates)

As fish are surrogates for vertebrates, the following conclusions apply equally to aquatic-phase amphibians. For freshwater fish, none of the RQs exceeded the LOC for acute or chronic exposures for all scenarios. However, RQs for chronic exposure to OXY under UV conditions exceeded the LOC of 1.0 for all scenarios. Although UV exposure in field water is expected to be more varied than under the laboratory conditions in which the endpoint was measured, risk cannot be precluded without additional UV exposure information. For site-specific scenarios, however, UV chronic risk may be mitigated by reducing the application rate to 0.5 lb/acre.

For saltwater fish, acute and chronic RQs for both paddy and release water exposure exceeded the LOC for standard soil scenarios. As the endpoint used for the acute assessments was non-definitive (LC50 > 11 μg/L) and concentrations in downstream waterbodies are expected to be lower than those in the paddy, uncertainty exists regarding the actual level of acute risk for saltwater fish. Nevertheless, acute risk to saltwater fish cannot be precluded. Chronic RQs for Davis and Biggs soil scenarios were 0.7 and 0.8, respectively. If saltwater fish were equally sensitive to OXY in the presence of UV light as freshwater fish (30x lower endpoint), calculated UV chronic RQs would be 21 and 24 for Davis and Biggs scenarios, respectively, exceeding the chronic LOC of 1.0. Risk conclusions for standard soil scenarios, however, would remain unchanged.

4.5.2.2 Invertebrates (water column)

Acute RQs for both paddy and release water exposure to freshwater invertebrates were below the LOC for all scenarios. However, chronic RQs exceeded the LOC for standard soil scenarios. A reduced application rate of 0.5 lb/acre was identified as sufficient to mitigate chronic risk. For saltwater invertebrates, acute and chronic RQs for both paddy and release water exposure exceeded the LOC for standard soil scenarios, with acute risks mitigated at reduced application rates (≤ 0.5 lb/acre). Presuming similar sensitivity to UV light as freshwater fish, calculated UV chronic RQs for both freshwater and saltwater invertebrates in the water column would exceed the chronic LOC of 1.0 for both Davis and Biggs soil scenarios. Risk conclusions for standard soil scenarios, however, would be unaffected.

4.5.2.3 Invertebrates (benthic)

For benthic freshwater invertebrates, acute and sub-chronic RQs for pore water exposure were below the LOC for all scenarios. However, chronic RQs for sediment exposure exceeded the LOC for all scenarios by 1x to 2x orders of magnitude, indicating a higher potential for risk from sediment exposure where concentrations of OXY are highest.

For benthic saltwater invertebrates, acute and chronic RQs for pore-water exposure exceeded the LOC for standard soil scenarios. These risks were mitigated at reduced application rates of 0.5 and 1.0 lb/acre for acute and chronic pore water risk, respectively. Chronic RQs for all scenarios exceeded the LOC for sediment exposure by 3x to 4x orders of magnitude. These results indicate greater risk from sediment exposure for saltwater benthic invertebrates, although uncertainty exists regarding the actual degree of dilution and exposure that is likely to occur for saltwater organisms.

4.5.2.4 Aquatic Plants

RQs for both paddy and release water exposure exceeded the LOC for vascular aquatic plants (vascular and non-vascular) for all scenarios. As such, conclusions of risk would not change for any scenario for aquatic plants if toxicity were enhanced by UV light. For site-specific scenarios, RQs for both paddy and release water exposure to non-vascular aquatic plants are below the LOC at a reduced application rate of 0.5 lb/acre. These results indicate that OXY applied to rice fields poses potential risk to aquatic plants and algae in general, both on the field and in downstream waterbodies, and under all lighting conditions.

4.5.3 Uncertainties

4.5.3.1 Use Patterns

Scenarios analyzed were developed based on typical use patterns for currently registered OXY-based products, and specific pesticide application methods, rates, and schedules were selected based on current herbicide programs for OXY-tolerant rice strains (K. Al-Khatib, personal communication, October 16, 2023). They are hypothetical and may differ from those specified in a pesticide label developed for use of OXY with California rice. Such changes have the potential to affect risk outcomes, creating uncertainty regarding the risk of OXY products approved for use on rice. However, the effects of reduced application rates (0.5 and 1.0 lb/acre) have been characterized and calculation of RQs at other application rates can be accomplished via the data presented in this study.

4.5.3.2 Use Sites

Three (3) soil conditions were evaluated: standard California soil conditions developed by the USEPA, and those representative of rice fields in Davis, CA and near Biggs, CA. These conditions may not be fully representative of all rice fields in California. However, the f_{oc} of the soils assessed in this study (1.0–2.41%) are similar to the range observed in California rice fields (1.19–2.52%).[16] Soil organic matter (SOM) is considered the most influential soil property governing partitioning of hydrophobic organic chemicals (such as OXY), and f_{oc} has been shown to be one of the most sensitive parameters for similar aquatic pesticide models, such as the PWC.[18-19, 26] Thus, the simulated scenarios may reasonably represent an appreciable range of California rice field conditions for modeling purposes.

4.5.3.3 Site-specific Degradation

Degradation rates specific to California rice fields were not available in the literature at the time of this assessment. If OXY was more recalcitrant in rice fields, EECs would be higher than those predicted in this analysis, potentially altering risk outcomes. To evaluate the potential impacts of increased persistence, a supplementary set of scenarios were run in which the 30-day water holding scenarios (S-30, D-30, and B-30) were simulated without any degradation (ESI2). EECs increased by 70 to 80% for the standard soil scenario, while EECs for site-specific soil scenarios increased by approximately 200%. In general, these increases did not affect risk outcomes for any receptor, except aquatic vertebrates. Without degradation, the chronic RQ for freshwater fish exceeded the LOC in the standard soil scenario, while both acute and chronic RQs exceeded the LOC for site-specific scenarios. Overall, these results suggest that the scenarios simulated are relatively insensitive to increased persistence. Thus, incorporation of degradation rates specific to California rice fields is unlikely to lead to additional conclusions of risk with the potential exception of risk to aquatic vertebrates.

4.5.3.4 UV Enhanced Toxicity

A UV enhanced toxicity endpoint was only available for freshwater fish. However, the chronic toxicity of OXY under UV conditions may be enhanced for all receptor groups. For freshwater fish, the UV chronic endpoint was approximately 30x lower than the endpoint under normal laboratory light conditions. If toxicity was enhanced by the same degree for other taxa, calculated RQs would be above the LOC for all scenarios and aquatic receptors. However, exposure to UV under artificial laboratory conditions may be substantially different than those in the natural environment, where light is affected by time of day, season, and atmospheric conditions, and both water depth and turbidity affect its penetration.[10] Exposure to UV within the environment may be inconsistent and dependent on receptor behavioral patterns. Thus, substantial uncertainty exists regarding the environmental relevance of UV chronic assessments and risk within the natural environment.

4.5.3.5 Hysteresis & Persistence

Partitioning between sediment and water column is simulated by PFAM as a completely reversible process.[24] However, currently available data for soil-water partitioning of OXY in California rice field soils suggest that OXY is poorly desorbed from rice field soil and exhibits sorption-desorption hysteresis.[17] Thus, environmental concentrations and behavior of OXY may differ from those predicted in this analysis.

Pesticides irreversibly sorbed to soil are typically less bioavailable for microbial degradation and more likely to accumulate, leading to persistence.[27] They are also more resistant to entering the water column where OXY is anticipated to dissipate the fastest. These features suggest that environmental water column concentrations may be lower than predicted while sediment concentrations may be higher. Consequently, risk from aqueous exposures may be lower than predicted. Risk conclusions from exposure to sediment, however, would be unaffected.

4.5.4 Conclusions

Results indicate that OXY is likely to concentrate in sediments, with limited availability in the water column. Dissipation is anticipated to be slow and largely governed by the anaerobic metabolic rate. Consequently, water holding period is predicted to have little impact on paddy and release water concentrations. This was especially pronounced in scenarios simulating soil organic carbon and partitioning characteristics measured in California rice field soils.

Acute risk to aquatic animals was generally low in the water column. However, chronic risk to freshwater fish under UV conditions, risk to aquatic plants, and chronic risk to benthic organisms exceeded assessment thresholds under all conditions evaluated. Risk to all receptors was also elevated in standard soil scenarios, which simulated lower f_{oc} and K_{oc} conditions.

Conversely, scenarios simulating California rice field soil conditions were associated with less overall risk and no acute risks to aquatic organisms. Risk conclusions from exposure to both paddy and release water were unaffected by water holding time for all scenarios.

These results suggest that the benefits of extending holding time may be limited for OXY and other means to address risk, such as reduced application rates or frequency, may be more effective. Thus, specification of a standard water holding period for OXY should be balanced with the needs of growers. Given that persistence may be a greater concern in California rice field soils, environmental monitoring is also recommended to evaluate the potential for OXY to accumulate in soils and sediments when applied in rice fields.

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Chapter 5

Conclusions

The environmental fate of oxyfluorfen (OXY) in rice fields was elucidated under simulated California rice-growing conditions. Fate processes were characterized via experimental determination of its soil-water partitioning behavior in two California rice field soils, calculation of Henry's law constant (K_H) and its temperature dependence, and calculation of environmental concentrations and effective compartment half-lives as summarized in Figure 5.1 using results for application scenario D-00 as a representative case.

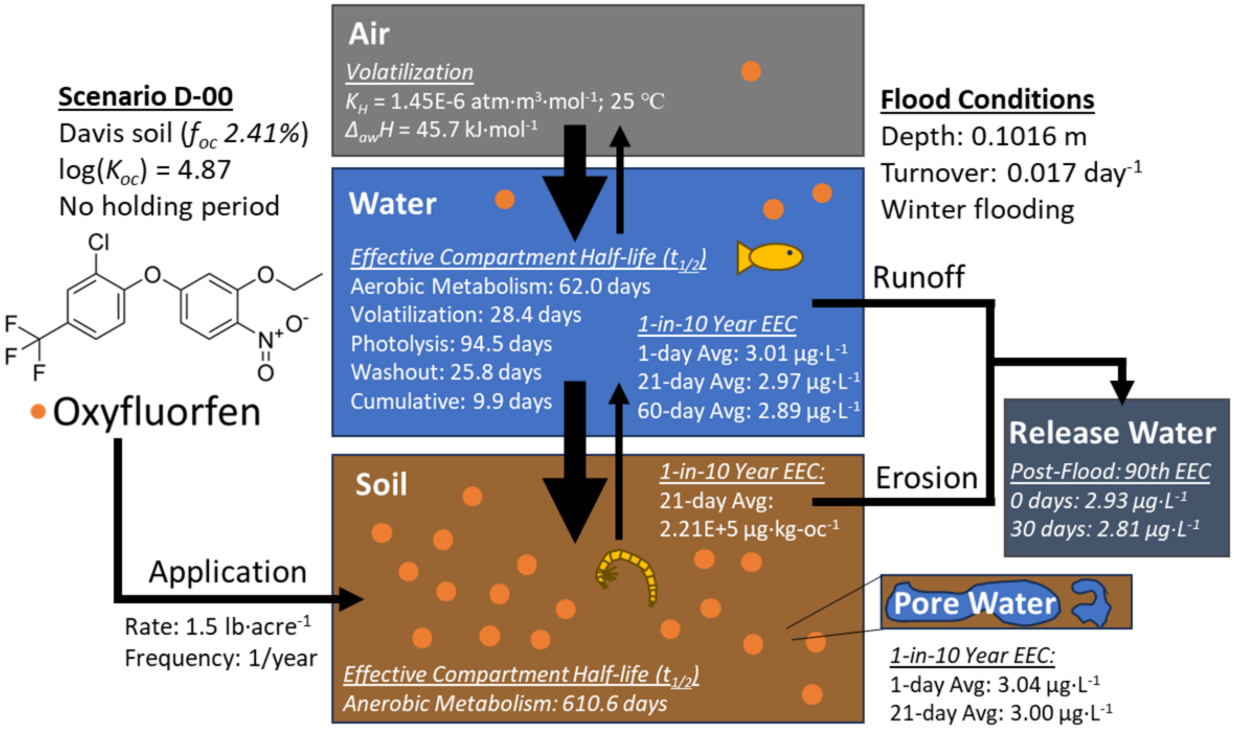

Figure 5.1 Summary of the environmental fate of oxyfluorfen under simulated California rice field conditions for application scenario D-00

OXY displayed high sorption affinity for rice field soils (log[Koc] 4.79–5.19) that was significantly enhanced by temperature, correlated with soil organic carbon, and predominantly concentration-independent (N 0.87–1.08) across all soil, temperature, and salinity treatments.

These results indicate that OXY is hardly mobile to immobile in soil and unlikely to leach into groundwater when used in rice fields. OXY did not readily desorb from soil once bound (9.3 to 27.0% desorption) and displayed significant sorption hysteresis (HI > 0) in all treatments. HI decreased with increasing rice field salinity, suggesting that sorption reversibility may vary between rice field locations and with evapoconcentration of salts. Overall, results suggest that OXY will concentrate in the sediment and be resistant to release into California rice field water.

A screening method was developed to evaluate the feasibility of experimental determination of Henry's law constant (K_H) via the gas-stripping method (GSM) for OXY. Results indicate that K_H cannot feasibly measured for OXY ($t_{strip} \geq 78$ days). Thus, K_H and its variability with California rice field temperature (5 to 40 °C) were calculated using four air-water partitioning models. Three (3) of the four models (EPI Suite, Kühne, and Two-Point Extrapolation) agreed that OXY is likely to be slightly volatile (K_H 3.00E-07−1.00E-05 $\text{atm}\cdot\text{m}^3\cdot\text{mol}^{-1}$) at most rice field temperatures (15−40 °C) and nonvolatile ($K_H <$ 3.00E-07 $\text{atm}\cdot\text{m}^3\cdot\text{mol}^{-1}$) at low temperatures (5−10 °C). In contrast, a single model (AQUAFAC-Sepassi) suggested that OXY is substantially volatile ($K_H >$ 1.00E-05 $\text{atm}\cdot\text{m}^3\cdot\text{mol}^{-1}$) under all rice field temperature conditions. However, investigation showed the model predicted key physical properties less accurately for OXY, suggesting less reliable results. Thus, the predominance of evidence suggests that OXY is nonvolatile to slightly volatile in California rice fields.

Estimated environmental concentrations (EECs) of OXY were calculated based on anticipated use patterns and water management practices in California using the Pesticides in Flooded Applications Model (PFAM) under two (2) California rice field soil conditions and one standard soil condition. OXY was highly concentrated in sediment (21-day Avg Benthic Sediment EEC: 220,747−411,000 µg/kg-oc) with limited availability in the water (21-day Avg

Water Column EEC: 2.97−31.4 µg/L). Dissipation was slow and largely rate limited by anaerobic microbial metabolism in the sediment, with an effective sediment compartment half-life of 610.6 days for all treatments. Although water column dissipation was comparatively rapid (Cumulative Effective Water Column Half-life: 9.4−10.5 days), the limited availability of OXY in water weakened the overall contribution of water column dissipation pathways. Overall, water holding period had little effect on paddy and release concentrations. These results suggest that OXY may accumulate in the soil over time leading to chronic exposure conditions for wildlife as more label fractions of bound residues release into overlying water.

Calculated EECs were used to characterize exposure and risk to aquatic receptors in accordance with ecological risk assessment guidelines. Short-term (acute) risk was generally low for water column dwelling animals (fish and water column invertebrates) and sediment dwelling (benthic) invertebrates. However, long-term (chronic) risk to freshwater fish (surrogates for aquatic-phase amphibians) under ultraviolet conditions, chronic risk to benthic invertebrates, and risks to aquatic plants & algae exceeded levels of concern for all scenarios. Scenarios simulating California rice field soil conditions were associated with less overall risk than standard soil conditions and indicated that the acute risks of OXY to aquatic animals was generally low (RQ < 0.1). Risk conclusions for all scenarios were unaffected by water holding periods up to 30 days.

Overall, this analysis suggests that benefits of extended holding periods are limited for OXY and other means to mitigate risk, such as reduced application rates or frequency, may be more effective. Thus, specification of water holding periods should be balanced with water management needs of growers. Environmental monitoring is also recommended as accumulation and persistence are major concerns for OXY when it is applied to California rice field soil.