Enhancement and inhibition of oxidation in phenolic compound mixtures with manganese oxides

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Abstract

Phenolic compounds can be oxidized by manganese oxides in the subsurface or during passive treatment of stormwater runoff and wastewater effluent. Contaminated waters may contain a complex mixture of phenolic compounds and these mixtures may have additive, synergistic, or antagonistic toxicological effects. However, the effects of such mixtures on the rates and mechanisms of phenol oxidation by manganese oxides are not well understood. This study addresses this knowledge gap by determining pseudo-first-order oxidation rates and oxidation mechanisms for four phenols reacted with δ-MnO_2 in varying mixtures. Oxidation rates of electron transfer-limited phenols (i.e., triclosan, resorcinol, bisphenol A) are inhibited in mixtures. This inhibition, as well as the observed decrease in sorption, is consistent with competition between phenols occurring near the Mn surface. In contrast, the oxidation rate and extent of sorption for sorption-limited 4,4’-biphenol is enhanced in mixtures. The rate enhancement is partially driven by indirect oxidation through radical-mediated reactions, likely from phenoxy radicals produced when electron transfer-limited phenols react with δ-MnO_2. These findings demonstrate that mixtures have a large impact on phenol oxidation by manganese oxides as the electron transfer-limited phenols are inhibited due to competition interactions and the sorption-limited phenol has increased oxidation rates due to indirect oxidation by radicals and enhanced sorption.

Keywords

Manganese oxides, phenolic contaminants, water treatment, kinetics.

Synopsis

This study investigates how phenol mixtures influence their reaction with manganese oxides, which is important for predicting reactivity in this water treatment system.

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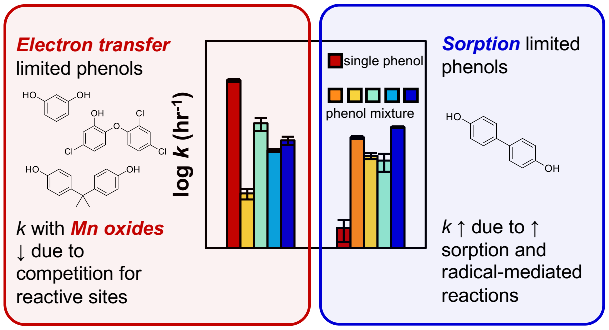

Introduction

Phenolic compounds are abundant in surface waters and encompass a variety of contaminant classes, including antimicrobial agents (e.g., triclosan), antioxidants (4,4'-biphenol), industrial chemicals (e.g., bisphenol A; BPA), and pharmaceuticals (e.g., resorcinol; **Table 1**).[1-4] These compounds may be released to surface waters in wastewater effluent, runoff, landfill leachates, and other waste streams.[3-12] In these systems, phenolic contaminants may impact ecological and human health through multiple toxicological effects, including endocrine disruption and bioaccumulation.[5, 11-17] Contaminants are frequently present as mixtures in aquatic systems, which influences both their removal efficiency in water treatment processes and their toxicity. For example, toxicological effects (e.g., estrogen production or inhibition) of phenolic contaminants depend on both contaminant concentration and competition between multiple phenols.[13, 16-18]

Manganese (Mn) oxides, are ubiquitous, redox active minerals, that oxidize phenolic contaminants in natural and engineered systems. Manganese oxides are formed naturally, generated as byproducts of engineered systems (e.g., drinking water treatment or acid mine drainage remediation), or synthesized for water treatment applications. These reactive minerals can therefore oxidize phenolic compounds in environmentally relevant systems (e.g., in soils or at the sediment-water interface)[1, 19-23] or be applied in passive *in situ* treatment systems.[2, 3, 6, 8, 10, 24-26] δ-MnO_2, a synthetic proxy for biogenic birnessite,[27] readily oxidizes many phenolic contaminants of interest including estrogens, bisphenol A, and other endocrine disruptors with demonstrated toxicological effects.[1, 2, 9, 21, 28-33] The oxidation of phenols by Mn oxides occurs through two stepwise single electron transfer reactions that form phenoxy radicals as intermediates and may be rate-limited by either sorption of the contaminant to the Mn surface or the first single electron transfer.[1, 2, 32, 34, 35] The rate limiting step of oxidation depends on both phenolic compound structure and Mn oxide characteristics in isolated batch reactions,[2] but the influence of competing phenolic contaminants on the mechanism and rate of oxidation by Mn oxides is unknown.

Understanding the interaction of multiple phenols with Mn oxides is critical for applying these minerals to oxidize contaminants in environmentally relevant waters for several reasons. First, phenols are typically present in mixtures in stormwater or in wastewater, yet nearly all studies on phenol reactivity with Mn oxides focus on individual compounds.[1] A single study on bisphenol A and diuron reactivity in a birnessite-coated sand column focused on optimizing design parameters as a function of background water chemistry,[6] while a study on multiple contaminants in a biochar-manganese oxide flow through system found sorption and biodegradation, rather than oxidation by Mn oxides, to be the dominant removal processes under the study conditions.[7] We are unaware of previous studies that consider the impact of mechanistic changes or compound-specific effects in phenol mixtures reacted with Mn oxides. Second, the oxidation of phenols by Mn oxides typically generates phenolic oxidation products;[14, 28, 36-39] competition between parent compounds and their products may partially explain changes in oxidation rates or sorption as the reaction proceeds.[28] Finally, model compound studies may provide insight into the reactivity of dissolved organic matter (DOM) with Mn oxides because this complex mixture contains numerous phenolic moieties.[40, 41] High-resolution mass spectrometry analysis of DOM demonstrates that lignin-like molecules, which are typically electron rich and likely phenolic in nature, are selectively oxidized by Mn oxides.[42, 43]

This study investigates the effect of mixtures on the initial kinetics and rate limiting steps of phenol oxidation by δ-MnO_2. Four phenols with differing functional groups, toxicological effects, and mechanisms of oxidation by Mn oxides[2] are used in this study. Both single compounds and mixtures are examined to determine how the rate limiting step and phenol structure alter the oxidation process in the presence of other compounds. Additionally, to determine the role of indirect oxidation by potential phenoxy radical products, selected experiments are conducted in the presence of a non-specific radical quencher, *tert*-butanol. The mechanistic results presented in this study have important implications for predicting the efficacy of manganese oxide-based treatment systems for degradation of contaminant mixtures.

Materials and Methods

Materials. Commercial chemicals were used as received. Ultrapure water was supplied by a Milli-Q water purification system maintained at 18.2 MΩ·cm. Bisphenol A, triclosan, resorcinol and 4,4'-biphenol stock solutions (5 mM) were prepared in methanol and stored at 4 °C. Further details are provided in Supporting Information (**Section S1**).

δ-MnO_2 synthesis and characterization. δ-MnO_2 was synthesized by a modified Murray method by adding $Mn(NO_3)_2$ dropwise (1 mL min^{-1}) into a mixture of $KMnO_4$ and NaOH at a molar ratio of 3:2:4 Mn^{II}:Mn^{VII}:OH^-.[2, 33, 44] The slurry was stirred for 20 hours and solids underwent three rounds of centrifuge washing at 2500 rpm for 15 minutes in Milli-Q water, followed by two centrifuge washings in pH 5.5 10 mM sodium acetate buffer. Reactions were started using this slurry within two days of δ-MnO_2 synthesis to minimize effects of mineral aging.

The average manganese oxidation number (AMON) of the δ-MnO_2 starting material was determined by oxalate titration to be 3.92 ± 0.05.[2, 45, 46] A similar AMON of 3.86 ± 0.04 was determined by X-ray absorption near edge structure (XANES) spectroscopy (Mn K edge; 6532 eV).[47] Specific surface area was determined by Brunauer–Emmett–Teller measurements (Quantachrome Autosorb-1, nitrogen adsorbate; 30 °C) and was 169 m^2/g for the starting material (**Table S1**). Aqueous manganese concentration, as well as solid-phase sodium content, were quantified by inductively coupled plasma-optical emission spectrometry (ICP-OES; Perkin Elmer 4300). Additional details on manganese oxide synthesis and characterization methods are presented in **Section S2**.

Kinetic studies. Resorcinol, bisphenol A, triclosan, and 4,4'-biphenol were reacted with δ-MnO_2 (15 mg-Mn/L) in triplicate batch reactors. These compounds were selected based on their rate limiting step and expected differences in reactivity,[2] as well as their environmental relevance. Reactions of single compounds with δ-MnO_2 were performed using phenol concentrations of 10, 20, or 40 μM (<0.1% MeOH in the final solution) to investigate concentration effects and to serve as controls for mixture reactions. The four phenols were also reacted with δ-MnO_2 in each possible paired combination (10 μM each, 20 μM total phenol) and in a mixture of all four phenols (10 μM each, 40 μM total phenol). All reactions were conducted in 10 mM sodium acetate buffer at pH 5.5 (total solution volume = 55 mL). This buffer was selected because it does not reduce or complex δ-MnO_2,[2]{Balgooyen, 2019 #5878} in contrast with Good's buffers and phosphate.{Balgooyen, 2019 #5878}{Klausen, 1997 #2559}{Yao, 1996 #3445} {Rubert, 2006 #2705}{Ouvrard, 2002 #6515} pH 5.5 was selected to enable comparison with previous work[2] and because it is below the acid dissociation constants (pK_a) of all considered phenols (**Table 2**). Solution pH changed less than 0.5 units during reactions. Rates of phenol oxidation by manganese oxides are pH dependent;[1, 20, 48] these four compounds react with δ-MnO_2 at pH 5.5 on a timescale of hours to days. Reactors were continuously stirred for up to 7 days in the dark.

Two aliquots were collected at each timepoint from triplicate reactors. One aliquot was filtered (1 mL; 0.2 μM PTFE syringe filters) and one aliquot was quenched (30 μL; 5:1 ascorbic acid:Mn molar ratio) to quantify aqueous and total phenol concentrations, respectively. Phenol concentrations were quantified by high performance liquid chromatography (**Section S3**).

Ascorbic acid-quenched aliquots, in which δ-MnO_2 is dissolved to release sorbed organic compounds, were used to calculate initial pseudo-first-order rate constants. A pseudo-first-order fit was used because manganese is in excess and because linear pseudo-first-order kinetics were typically observed over the initial reaction period (i.e., <100 min for triclosan, bisphenol A, and resorcinol; <1,400 min for 4,4'-biphenol; **Figure S2**). Phenol concentrations in filtered aliquots were subtracted from quenched aliquots to determine the fraction of each compound sorbed to the Mn surface at each timepoint. Phenols with observed maximum sorption <10% or with error greater than the average measured sorption were designated sorption-limited, as validated previously.[2] Compounds with a maximum observed percent sorption >10% were classified as electron transfer-limited.

The 10 μM isolated reactions, paired reactions, and mixture of all four phenols with δ-MnO_2 were repeated in the presence of 2 mM *tert*-butanol, a non-specific radical quencher,[49-53] to determine the effect of product phenoxy radicals on oxidation rates and mechanisms. The presence of *tert*-butanol and the acetate buffer did not alter initial δ-MnO_2 characteristics (i.e., AMON and surface area; **Section S2**).

Results and Discussion

The oxidation rates of four phenolic contaminants (resorcinol, 4,4'-biphenol, bisphenol A, and triclosan) by δ-MnO_2 are quantified alone, in pairs, and in mixtures of all four phenols. This allows us to determine if the mixture of phenolic compounds leads to enhancement or inhibition of reaction rates. Resorcinol, triclosan, and bisphenol A are electron transfer-limited and 4,4'-biphenol is sorption-limited with δ-MnO_2 based on previous research using the same Mn oxide under similar reaction conditions (**Table 1**).[2] Since the extent of sorption plays a large role in determining the rate and mechanism of phenol oxidation,[2] we hypothesize that all four phenols will have slower pseudo-first-order oxidation rates and less sorption due to competition effects in mixtures. Furthermore, we hypothesize that these competition effects will impact the oxidation of slower reacting and sorption-limited phenols (e.g., 4,4'-biphenol) to a greater extent than the more reactive, electron transfer-limited phenols (e.g., resorcinol).

Reactivity of individual phenols. Overall, the pseudo-first-order phenol oxidation rates follow the order of resorcinol > bisphenol A > triclosan >> 4,4'-biphenol in isolated reactions with δ-MnO_2 (**Figures 1a** and **2a**). Resorcinol, bisphenol A, and triclosan sorb strongly (average sorption for the three compounds and three concentrations = 82.7 ± 20.9%; **Figure 1b**) due to rapid formation of precursor complexes with the Mn surface and are therefore electron transfer-limited with δ-MnO_2.[2] The oxidation of 4,4'-biphenol is sorption-limited and reacts at a rate that is several orders of magnitude lower than the other three phenols ($t_{1/2}$ = 223.6 hours for 4,4'-biphenol vs. $t_{1/2,average}$ = 0.09 ± 0.03 hours for the other phenols at an initial concentration of 10 μM).

The observed reactivity trends are not well explained by parameters frequently used in quantitative structure-activity relationships (QSARs) to relate phenol reactivity with Mn oxides (**Table 2**). For example, energy of the highest occupied molecular orbital (E_{HOMO}) and oxidation potential (E_{ox}) describe the susceptibility of a compound to oxidation. Electron loss from a molecule with a higher E_{HOMO} is more favorable and thus is expected to have higher oxidation rates. Conversely, higher E_{ox} values indicate the molecule takes more energy to oxidize and thus is expected to have lower oxidation rates. Similarly, the presence of electron-withdrawing substituents, corresponding to higher Hammett constants or lower pK_a values, should result in lower oxidation rates. These trends are corroborated by surveys of these reactivity constants versus phenol oxidation rates and mechanisms by Mn oxides.[2, 54, 55] While it is not valid to develop QSARs for four compounds, the available data result in trends that are opposite the expected QSAR relationships. For example, 4,4'-biphenol (i.e., the slowest reacting compound) has the highest E_{HOMO} value, second lowest E_{ox} value, and second lowest pK_a (**Table 2**); these parameters indicate that the compound should be highly reactive. However, QSARs are most accurate for simple phenols with *meta*- and *para*-substituents and large deviations are observed for phenols with *ortho*-substituents (e.g., resorcinol) and for more complex phenols (e.g., triclosan, bisphenol A, and 4,4'-biphenol).[2] Therefore, it is unsurprising to see variable trends among these four specific compounds.

In addition to 10 µM isolated reactions of each phenol with δ-MnO_2, we analyze the extent of sorption and oxidation rate for initial concentrations of 20 and 40 µM of each individual compound with δ-MnO_2. These concentrations correspond to the total initial phenol concentration in isolated reactions, paired mixtures, and a combination of all four phenols in solution, respectively. Therefore, evaluating the impact of initial phenol concentration on its reactivity allows us to confirm that changes in pseudo-first-order rate constants and sorption in experiments containing multiple phenols are the result of mixture effects rather than differences in the total phenol concentration.

Initial concentration does not impact the rate constant or mechanism of oxidation for resorcinol, bisphenol A, or triclosan, which are electron transfer-limited compounds that react rapidly with δ-MnO_2 (**Figure 1**). However, initial concentration significantly influences the reactivity of 4,4'-biphenol with δ-MnO_2 (p-value = 0.039). Sorption of 4,4'-biphenol increases from 28 ± 29% to 56 ± 32% as the initial phenol concentration increases from 10 to 40 µM. The increase in extent of sorption indicates a mechanism change from sorption-limited at initial concentrations of 10 and 20 μM (i.e., due to the large error and observed kinetic behavior) to electron transfer-limited at 40 μM. This shift in the rate limiting step of reaction is accompanied by an increase in 4,4'-biphenol oxidation rate from 3.1 x 10^{-3} hr^{-1} to 7.2 x 10^{-3} hr^{-1}. Despite the increase in oxidation rates between 10 and 40 μM of 4,4'-biphenol (**Figure 1**), the differences in oxidation rate and extent of sorption are much less than those observed in the contaminant mixtures described below. Therefore, these results indicate that changes in pseudo-first-order oxidation rates, sorption, and reaction mechanism are primarily attributable to effects stemming from the mixtures, rather than simply the change in overall phenol concentration.

Impacts of mixtures on electron transfer-limited phenols. Reacting the three electron-transfer limited phenols (i.e., triclosan, bisphenol A, and resorcinol) with δ-MnO_2 in the presence of a second phenol or in a mixture of all four phenols results in consistent decreases in both oxidation rates and sorption. Because the oxidation rate of these compounds is independent of initial phenol concentration in single-phenol experiments (**Figure 1a**), the observed changes in reactivity are attributable to effects of the other phenols. Triclosan is oxidized at rates of 4.8, 6.7, and 2.7 times slower with bisphenol A, 4,4'-biphenol, and resorcinol, respectively, compared to the 10 μM isolated triclosan control, with decreases in triclosan sorption up to 47% in these mixtures (**Figure 2**). Triclosan is electron transfer-limited in all reactions and the decreases in rate and sorption suggest competitive interactions between compounds for Mn surface sites.

As observed with triclosan, the decreases in apparent oxidation rates and extent of sorption of bisphenol A and resorcinol are consistent with competition in these mixture solutions (**Figure 2**). Bisphenol A oxidation is 2 – 4 times slower in solution with triclosan and 4,4'-biphenol and 8.4 times slower in solution with all four phenols, while bisphenol A sorption in these reactions decreases by up to 25%. The oxidation rate of resorcinol also decreases in all mixtures compared to the 10 μM control (**Figure 2**). Triclosan, 4,4'-biphenol, and mixtures of all four phenols together result in 10 – 50 times lower oxidation rates and 2 – 3 times lower sorption of resorcinol. Although the extent of sorption decreases, bisphenol A and resorcinol remain electron-transfer limited in the presence of triclosan or 4,4'-biphenol.

Interestingly, the combination of bisphenol A and resorcinol results in much slower oxidation rates and a mechanism change for both compounds. This mixture results in large decreases in sorption for both bisphenol A (8% versus 100%) and resorcinol (7% versus 49%; **Figure 2b**), indicating that the oxidation mechanism of both compounds becomes sorption-limited when these phenols are combined. This change in mechanism is accompanied by dramatically slower apparent oxidation rates (i.e., 56 times lower for bisphenol A and three orders of magnitude lower for resorcinol; **Figure 2a**).

The simultaneous decrease in both resorcinol and bisphenol A reactivity indicates that resorcinol does not outcompete bisphenol A, which might be expected based on the faster isolated kinetics of resorcinol (**Figure 1**). Instead, these data demonstrate that oxidation of both phenols is inhibited when together in solution with δ-MnO_2. The simultaneous shift to a sorption-limited reaction mechanism for both compounds indicates that resorcinol and bisphenol A are competing for reactive sites and that they react rapidly upon sorption to the δ-MnO_2 surface. The extent of sorption is low for both phenols (15% combined) compared to isolated reactions or other mixtures analyzed. Therefore, it is likely that physical blocking of unfilled reactive sites prevents sorption of these contaminants as δ-MnO_2 has enough surface sites to support 100% sorption of compounds in reactions with the same initial phenol concentration (**Figure 1**).

These results suggest that apparent oxidation rates of phenolic contaminants which are electron transfer-limited with δ-MnO_2 are inhibited because competition for reactive surface sites decreases sorption to the Mn surface. The extent of inhibition is not predicted by either extent of sorption or pseudo-first-order oxidation rates in isolated studies as bisphenol A has the greatest percent sorption to δ-MnO_2 and resorcinol has the highest pseudo-first-order rate constant in isolated systems (**Figure 1**). Oxidation rates of bisphenol A and resorcinol are inhibited by mixtures with one another to the extent that they both become sorption-limited, while triclosan, which has neither the greatest sorption nor fastest oxidation, remains electron transfer-limited in all mixtures.

Since oxidation rates in these reactions depend on both precursor complex formation and reactivity with δ-MnO_2, predicting the outcome of these competitive interactions is complicated and depends on charge, oxidation potential, and partitioning behavior among other factors. The differential reactivity of the bisphenol A/resorcinol pair observed here cannot be solely explained by a single factor or physicochemical parameter. For example, similar inhibitory behavior of 4,4'-biphenol with resorcinol and bisphenol A would be expected if competitive electrostatic interactions contribute to decreased reaction rates since these compounds have nearly identical pK_a values and are therefore neutral at pH 5.5 (**Table 2**). Similarly, favorable partitioning to organic phases (e.g., a relatively hydrophobic, organic-loaded Mn surface) can be ruled out given the wide range of K_{ow} values and differential behavior of resorcinol, triclosan, and bisphenol A. While the three, electron transfer-limited phenols studied here each had varying physiochemical constants and reactivity in isolated solutions, it is important to note that all three are inhibited to some extent in all tested mixture combinations. Thus, these results are likely relevant for other phenolic contaminants which are electron transfer-limited under these conditions, such as chlorophenols, 4-nonylphenol, estrone, and 17β-estradiol.[2] Inhibition of sorption demonstrated for binary phenol mixtures and a range of sorbents has been attributed to hydrogen bonding, electrostatics, and overlapping pi orbital interactions.[56, 57] Our results suggest that such intermolecular competitive effects occur for the three, electron transfer-limited phenols in reactions with δ-MnO_2.

Impacts of mixtures on a sorption-limited phenol. Unlike the other three phenols, the rate of 4,4'-biphenol oxidation by δ-MnO_2 increases significantly in the presence of the other three phenolic contaminants ($p = 6.66 \times 10^{-5}$; **Figure 2**). For example, the 4,4'-biphenol oxidation rate increases by a factor of 42 in the presence of triclosan, a factor of 55 in the presence of bisphenol A, and a factor 152 in the presence of resorcinol (total phenol concentration = 20 μM). The largest increase in 4,4'-biphenol oxidation rate is observed in the solution containing all four phenols (total phenol concentration = 40 μM) in which the oxidation rate is 268 times higher compared to the rate observed when 10 μM 4,4'-biphenol reacts with δ-MnO_2 in the absence of other phenols. The large increase in 4,4'-biphenol oxidation rate is contrary to our hypothesis that sorption-limited phenols would undergo the largest decrease in oxidation in the presence of other phenols. Thus, these results indicate that competition does not inhibit 4,4'-biphenol oxidation as observed in the case of electron transfer-limited phenols, but instead suggest that another mechanism (e.g., enhanced sorption or radical-mediated reactions) increases the rate of 4,4'-biphenol oxidation in these mixtures.

Sorption of 4,4'-biphenol is 2 – 4 times greater in paired mixtures than in isolated reactions, resulting in its oxidation becoming electron transfer-limited rather than sorption-limited. A similar increase in sorption (i.e., a factor of 2) and shift in mechanism is observed in control experiments when the initial 4,4'-biphenol concentration increases from 10 to 40 μM (**Figure 1**), suggesting that the shift from sorption-limited to electron transfer-limited oxidation of 4,4-biphenol in these mixtures results from greater organic loading. However, this shift in mechanism does not fully explain the large increase in 4,4'-biphenol oxidation rate observed in phenol mixtures because the rate only increases by a factor of 2 in the 40 μM 4,4'-biphenol control in contrast with the >200 times increase observed when all four phenols are present as a mixture (total phenol concentration = 40 μM).

Because enhanced sorption is not the sole mechanism of increased 4,4'-biphenol oxidation rate, we evaluate the role of indirect oxidation by phenoxy radicals. As phenols are oxidized by δ-MnO_2, they form a phenoxy radical as the product of the first electron transfer. While phenoxy radicals are transient and difficult to observe,[58] thermodynamic and kinetic calculations show that the radical is a key intermediate in single electron oxidation reactions such as those involving Mn oxide mineral surfaces and phenolic compounds.[59] This radical may remain sorbed to the Mn surface and undergo a second electron transfer or diffuse from the surface and react in solution.[1, 2, 21, 32] For example, phenoxy radicals generated by the reaction of phenols with Mn oxides can undergo radical coupling to form polymeric hydroquinone-like products.[1, 2, 32] Polymeric product formation from bisphenol A oxidation is not dependent on initial concentration despite changes in bisphenol A oxidation rate and δ-MnO_2 reduction, suggesting that single-electron transfer reactions are linked to radical coupled polymeric products.[28] Similarly, studies of triclosan and chlorophene oxidation by manganese oxides link fast, electron transfer-limited reaction mechanisms with the formation of radical coupled dimer products identified by mass spectrometry.[48] Given these findings, resorcinol, bisphenol A, and triclosan are all likely to undergo a one electron transfer reaction at the Mn surface to form a phenoxy radical.[35] Thus, we investigate whether the phenoxy radicals produced as initial products of resorcinol, bisphenol A, and triclosan oxidation by δ-MnO_2 can react with 4,4'-biphenol, resulting in enhanced 4,4'-biphenol oxidation.

To test for oxidation by radical production in mixtures of the other three phenolic contaminants and 4,4-biphenol, we examined individual phenols, paired mixtures, and combinations of all four phenols in the presence of *tert*-butanol, a non-specific radical quencher that is not likely to react directly with Mn oxides[49-53] and does not alter the mineral surface (**Table S1**). Little change in oxidation rate is observed with *tert*-butanol in solution with triclosan, resorcinol, and bisphenol A both in isolation or in mixtures (**Section S7**). This suggests that secondary reactions of phenoxy radicals with these phenols are not responsible for oxidation of the parent compounds, confirming the assumption that direct electron transfer from δ-MnO_2 is the dominant oxidation mechanism for these three phenols. Similarly, the oxidation rate of 4,4'-biphenol by δ-MnO_2 in control experiments with and without *tert*-butanol is nearly identical (3.7×10^{-3} hr^{-1} and 3.1×10^{-3} hr^{-1}, respectively; **Figure 3a**), indicating that the presence of the radical quencher does not impact the direct oxidation of 4,4'-biphenol by δ-MnO_2.

The addition of *tert*-butanol to solutions containing mixtures of 4,4'-biphenol and other phenols consistently results in decreased 4,4'-biphenol oxidation rates compared to unquenched reactions (**Figure 3a**). The 4,4'-biphenol oxidation rate decreases by a factor of 1.3 when *tert*-butanol is added in the mixtures containing bisphenol A and a factor of 5.9 when the quencher is added to a solution containing all four phenols. The largest difference between quenched and unquenched reactions is observed when resorcinol is present (i.e., either the resorcinol and 4,4'-biphenol pair or the combination of four phenols), indicating that resorcinol-derived phenoxy radicals may be most reactive with 4,4'-biphenol. The decrease in 4,4'-biphenol oxidation rates in the presence of a non-specific radical quencher provides evidence for indirect oxidation of 4,4'-biphenol by phenoxy radicals generated by the other three phenols.

The relative change in 4,4’-biphenol oxidation rate in the presence and absence of the quencher varies among the different phenol combinations. However, it is noteworthy that the absolute 4,4’-biphenol oxidation rate in the presence of the radical quencher and other phenols is nearly identical (i.e., average for all 4,4’-biphenol competition experiments with *tert*-butanol = 0.11 ± 0.04 hr^{-1}; **Figure 3a**). Thus, the radical quencher decreases the 4,4’-biphenol oxidation rate to a consistent value regardless of the phenol mixture. However, the average radical quenched rate is still 30 times higher than the 4,4’-biphenol oxidation rate observed in the absence of other phenols, indicating that phenoxy radical-mediated reactions are not solely responsible for the enhanced 4,4’-biphenol oxidation rate observed in mixtures.

An examination of the amount of 4,4’-biphenol sorbed to the δ-MnO_2 surface reveals that the presence of 2 mM *tert*-butanol leads to enhanced sorption (**Figure 3b**). For example, sorption of 4,4’-biphenol to the δ-MnO_2 surface increases from 29 ± 28% to 81 ± 6% in unquenched and quenched 10 μM controls, respectively. Similarly, 4,4’-biphenol sorption in phenol mixtures increases from 46% to 76% (average of all mixture combinations) in the absence and presence of *tert*-butanol. Thus, this data suggests that the presence of *tert*-butanol alone influences 4,4’-biphenol sorption to a greater extent than the presence of other phenols. While *tert*-butanol does not react directly with Mn oxides or change the Mn oxide oxidation state or surface area (**Table S2**), it is possible that the high *tert*-butanol concentration results in favorable interactions between 4,4’-biphenol and a more organic-rich oxide surface. Therefore, the enhanced sorption of 4,4’-biphenol to the δ-MnO_2 surface due to *tert*-butanol partially counterbalances the effect of the radical quencher, emphasizing the importance of carefully interpreting results in heterogenous systems.

We conclude that there are two mechanisms contributing to the enhanced oxidation of the sorption-limited phenol (i.e., 4,4'-biphenol) by δ-MnO_2 in the presence of other highly reactive phenols. First, the data clearly indicate that the presence of additional organic compounds increases the extent of 4,4'-biphenol sorption to the mineral surface, likely through enhanced partitioning to an organic-rich surface. This is observed for 4,4'-biphenol in individual reactions (**Figure 1b**), in binary mixtures (**Figure 2b**), and in the presence of 2 mM *tert*-butanol (**Figure 3b**). While we focus our analysis on maximum sorption in order to identify shifts in mechanism, the presence of other organics may also influence the rate of sorption and partially contribute to enhanced 4,4'-biphenol oxidation rates. However, the fact that the 4,4'-biphenol oxidation rate only increases modestly in individual reactions (40 μM vs. 10 μM; **Figure 1a**) and is unchanged in the presence of 2 mM *tert*-butanol (**Figure 3a**) demonstrates that enhanced sorption does not fully explain the large increase in 4,4'-biphenol oxidation rate in the presence of other phenols. The ability of a non-specific radical quencher to decrease 4,4'-biphenol oxidation rates in mixtures indicates that radicals generated during the one electron oxidation of resorcinol, bisphenol A, and triclosan are involved, thus demonstrating the presence of a novel indirect mechanism of 4,4'-biphenol oxidation in this complex system.

Conclusion. Phenolic contaminants are frequently present as mixtures in the environment, which influences both their toxicity and their removal efficiency in water treatment processes. Studying the fate of mixtures is complicated due to the large number of possible contaminants. As a result, little is known about how contaminants interact in water treatment processes, including processes that use manganese oxides to oxidize phenols.

Depending on the phenolic contaminant of interest, oxidation by Mn oxides may be either enhanced or inhibited by mixture effects. In general, the studied electron transfer-limited contaminants, including resorcinol, BPA, and triclosan, have inhibited oxidation in mixtures due to competitive interactions with other compounds. In contrast, the sorption-limited phenol (i.e., 4,4'-biphenol) is oxidized more quickly in mixtures. Our evidence suggests the increase in 4,4'-biphenol pseudo-first-order oxidation rates results from a modest contribution of enhanced sorption to the mineral surface and, importantly, indirect oxidation by phenoxy radical products of other phenols in solution. This pathway is supported by observed product dependency on oxidation mechanisms in previous studies,[28, 48] as well as decreases in 4,4'-biphenol oxidation rates in the presence of *tert*-butanol here. Although product identification is necessary to further confirm this radical-mediated oxidation enhancement pathway, this study provides evidence of indirect oxidation in mixtures of phenolic contaminants by δ-MnO_2, highlighting the importance of mechanistic and kinetic studies of study complex mixtures.

These results are especially relevant for stormwater, wastewater, and landfill leachate which contain a wide array of phenolic contaminants and are primary candidates for treatment by manganese oxides.[4, 5, 8, 60-63] Electron transfer-limited contaminants, which generally have higher oxidation rates with manganese oxides compared to sorption-limited contaminants,[2, 34] will likely undergo less sorption and slower oxidation than observed in isolated solutions. In contrast, some slow reacting sorption-limited contaminants may have increased oxidative degradation in mixtures treated with manganese oxides.

While this study provides mechanistic insights into the complex interactions of individual phenols with manganese oxides, further research is needed on the role of dissolved organic matter in this complex system in order to assess efficacy and mechanism in treatment systems. The existing literature is contradictory and varying effects of DOM on organic compound transformation rates by manganese oxides have been reported. For example, DOM can decrease,[6,

[64] increase,[65] or have no effect[6, 66] on the oxidation rate of bisphenol A by manganese oxides. DOM contains phenols as redox active moieties[40-42, 67] and it is likely that variable DOM composition (e.g., total phenolic content and reactivity of individual phenolic moieties) contributes to differing effects observed in previous studies. This study demonstrates that individual model phenols result in different trends (i.e., competition or enhancement) and thus provides insight into the variable behavior observed when DOM (i.e., a complex mixture rich in phenolic moieties) is present.

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Supporting Information Available

Additional experimental details, manganese oxide synthesis methods, raw kinetic data, tabulated kinetic and sorption data, Figures S1-S3, and Tables S1-S11 are included in the Supporting Information.

Tables and Figures

Table 1. Chemical structure, contaminant class, and rate limiting step of oxidation by δ-MnO_2 of each phenolic contaminant.

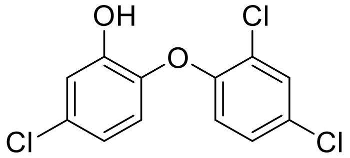
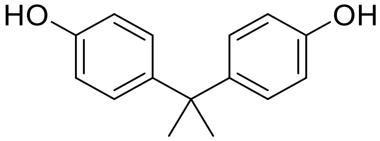
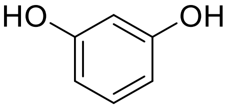
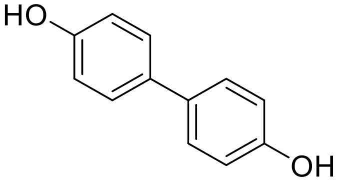
Phenol	Structure	Contaminant class	Rate limiting step
triclosan		antimicrobial agent	electron transfer-limited
bisphenol A		plastics production; endocrine disruptor	electron transfer-limited
resorcinol		pharmaceutical	electron transfer-limited
4,4'-biphenol		antioxidant	sorption-limited

Table 2. Structure-activity and partitioning constants for resorcinol, bisphenol A, triclosan, and 4,4'-biphenol. Constants include the acid dissociation constant (pK_a), energy of the highest occupied molecular orbital (E_{HOMO}), oxidation potential (E_{ox}), log of the octanol:water partitioning coefficient (log K_{ow}), and the pH adjusted value (log D_{ow}). Sources for each constant are given in subscript following the column heading.

	pK_a[48]	E_{HOMO} (eV)[2]	E_{ox} (V vs. SHE)[2]	log K_{ow}[48]	log D_{ow}[48]
resorcinol	9.26	-7.77	1.83	0.93	1.37
bisphenol A	9.78	-7.49	2.22	3.32	4.05
triclosan	7.68	-7.78	2.07	4.76	4.98
4,4'-biphenol	9.64	-7.23	1.82	2.80	3.01

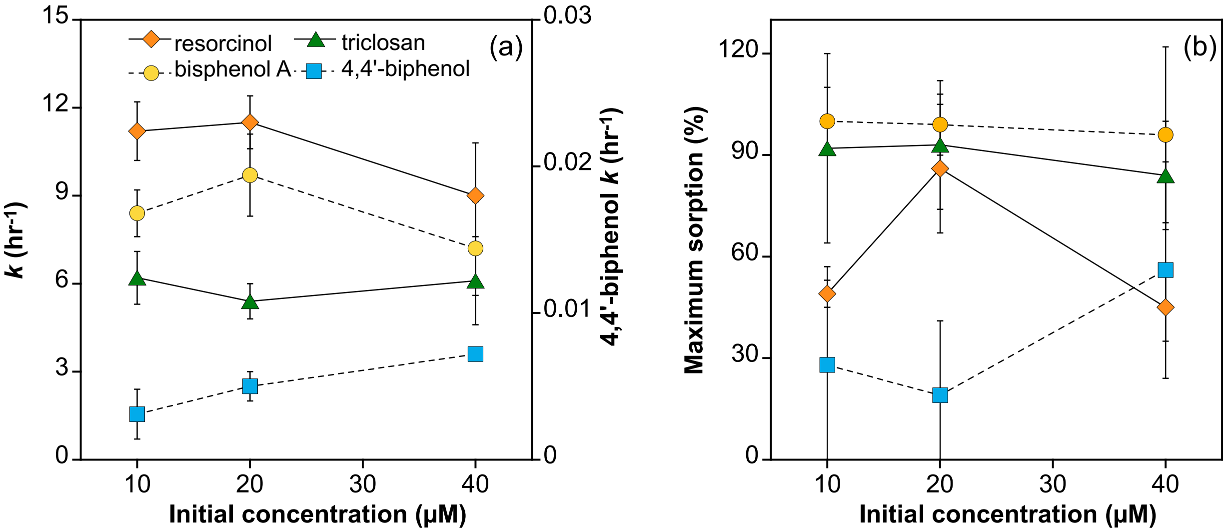


Figure 1. (a) Pseudo-first-order oxidation rates and (b) maximum percent sorption versus initial concentration of resorcinol, bisphenol A, triclosan, and 4,4’-biphenol reacted with δ-MnO_2 at pH 5.5. Error bars are ± 1 standard deviation of triplicate reactors. This data is tabulated in **Tables S3** and **S6**.

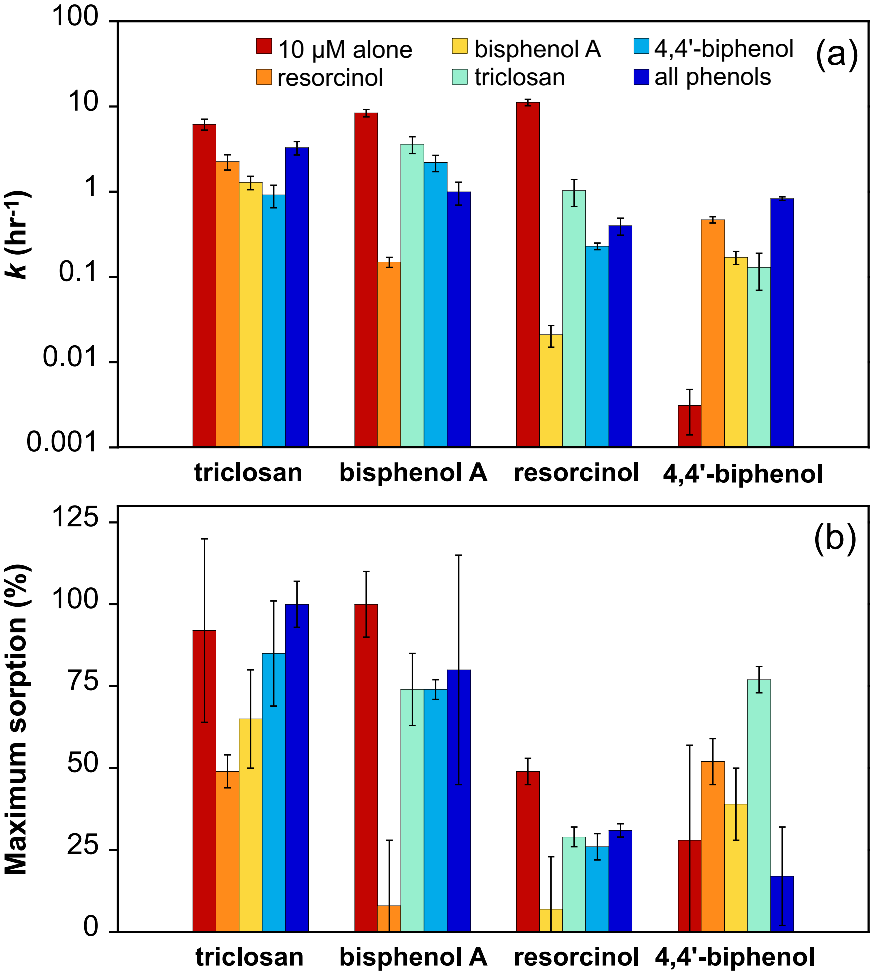


Figure 2. (a) Pseudo-first-order oxidation rates and (b) maximum percent sorption of resorcinol, bisphenol A, triclosan, and 4,4’-biphenol reacted with δ-MnO_2 at pH 5.5 in isolation or in mixture solutions with other phenolic contaminants. Error bars are ± 1 standard deviation of triplicate reactors. This data is tabulated in **Tables S4** and **S7**.

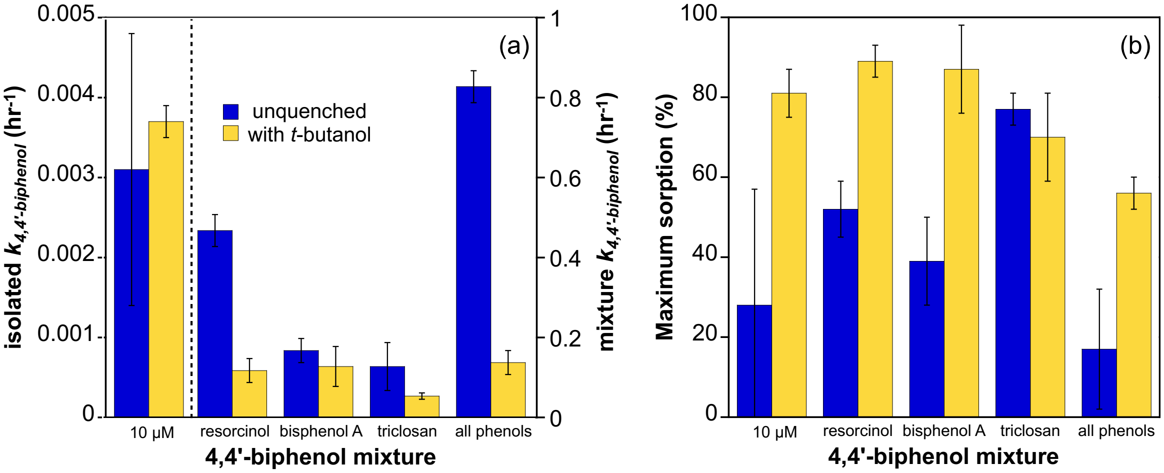


Figure 3. (a) Pseudo-first-order oxidation rates and (b) maximum percent sorption of 4,4'-biphenol reacted with δ-MnO_2 with and without 2 mM *tert*-butanol in solution. Bars correspond to 4,4'-biphenol without other phenols ($[\text{phenol}]_{\text{total}}$ = 10 µM), 4,4'-biphenol with 10 µM resorcinol, bisphenol A, or triclosan ($[\text{phenol}]_{\text{total}}$ = 20 µM), and 4,4'-biphenol with all other phenols ($[\text{phenol}]_{\text{total}}$ = 40 µM). Error bars are ±1 standard deviation of triplicate reactors. This data is tabulated in **Tables S5** and **S8**.

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