# Effects of Solution Chemistry on the Dechlorination of 1,2,3-Trichloropropane by Zero-Valent Zinc

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S *Supporting Information*

ABSTRACT: The reactivity of zerovalent zinc (ZVZ) toward 1,2,3-trichloropropane (TCP) was evaluated under a variety of solution conditions, including deionized water, groundwater, and artificial groundwater, over a pH range of about 6.5–12. In deionized water, first-order rate constants for TCP disappearance (k_{obs}) exhibit a broad minimum between pH 8 and 10, with increasing k_{obs} observed at lower and higher pH. The similarity between this trend and zinc oxide (ZnO) solubility behavior suggests pH related changes to the ZnO surface layer strongly influence ZVZ reactivity. Values of k_{obs} measured in acidic groundwater are similar to those measured in DI water, whereas values measured in alkaline groundwater are much smaller (>1 order of magnitude at pH values >10). Characterization of the surfaces of ZVZ exposed to deionized water, acidic groundwater, and alkaline groundwater suggests that the slower rates obtained in alkaline groundwater are related to the presence of a morphologically distinct surface film that passivates the ZVZ surface. TCP degradation rates in artificial groundwater containing individual solutes present in groundwater suggest that silicate anions contribute to the formation of this passivating film.
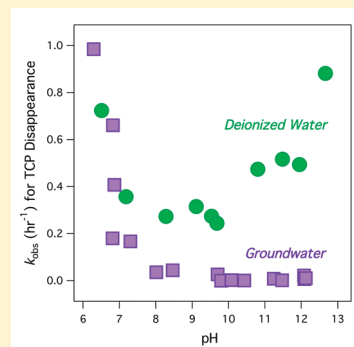
INTRODUCTION

1,2,3-trichloropropane (TCP) is an emerging contaminant that is "reasonably anticipated to be a human carcinogen".[1] Groundwater contamination with TCP occurs at industrial and agricultural sites due to its use as a solvent for degreasing, feedstock for polymer production, and as a precursor to (and impurity in) some soil fumigants. Recent cases, involving the closure of drinking water production wells due to TCP contamination above action levels,[2] have focused attention on TCP's unusual persistence and recalcitrance to common methods of remediation.[3] To provide a more complete understanding of the chemical transformation processes that determine the fate and potential for remediation of TCP, we have recently reported experimental and theoretical studies on the reactivity of this compound.[4,5] After consideration of TCP degradation by substitution, hydrolysis, reduction, and oxidation,[4] we concluded that reduction with zerovalent zinc (ZVZ) was particularly significant because it represents a novel and potentially promising method of affecting relatively fast TCP degradation.

While the ability of ZVZ to degrade chlorinated solvents has been described previously,[6−10] the advantages of ZVZ over the more conventional and better-characterized zerovalent iron (ZVI) have not been sufficient to generate interest in field-scale applications of ZVZ for remediation of contaminated groundwater. In the case of TCP, however, our results suggest that the kinetic advantage of ZVZ over ZVI is such that ZVZ has potential for remediation of TCP while ZVI does not.[4]

To assess the prospects for TCP remediation with ZVZ under field conditions, we have begun to consider (i) the use of less

pure, and therefore less expensive, ZVZ; (ii) treatment under flow-through conditions (columns); and (iii) the effects of solutes found in groundwater. We reported results on (i) and (ii) previously;[11] here we describe results that address (iii). The focus of this work is on the effect of solution chemistry— including that of artificial and real groundwater—on the kinetics of TCP degradation using commercial-grade ZVZ. In addition to assessing the reactivity of ZVZ under conditions better reflective of the field, we have attempted to reconcile this reactivity data with information from the literature on zinc corrosion and the mechanism of its passivation.

ZVZ corrodes in deionized (DI) water to form zinc oxide (ZnO) and/or zinc hydroxide ($Zn(OH)_2$).[12,13] These phases are amphoteric, displaying minimum solubilities at approximately pH 9, with solubility increasing at lower and higher pH (producing "U"- or "V"-shaped solubility diagrams).[13] Zinc (hydr)oxide corrosion products are present as surface films between pH 6 and 12[14] and—depending on their structure— may inhibit further corrosion, resulting in passivation. These films have been extensively studied under alkaline conditions where they have been classified into two types, "type I" and "type II".[12,15,16] Type I is bulky and porous and permits continued corrosion of the metal, while type II is thin and more compact and limits corrosion, causing a transition from active to passive states.[12,15,16]
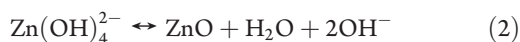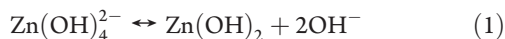
Type I films consist of either $Zn(OH)_2$ or ZnO formed by reprecipitation of dissolved Zn^{2+} species according to eqs 1 and 2.[15]

$$Zn(OH)_4^{2-} \leftrightarrow Zn(OH)_2 + 2OH^- \qquad (1)$$

$$Zn(OH)_4^{2-} \leftrightarrow ZnO + H_2O + 2OH^- \qquad (2)$$

As the type I film forms, it limits access of hydroxide to the ZVZ surface and promotes the formation of the type II film, which results directly from oxidation of the metal surface, according to eq 3.[15]

$$Zn + 2OH^- \leftrightarrow ZnO + H_2O + 2e^- \qquad (3)$$
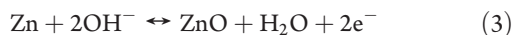
Type II films consist of zinc-rich zinc oxides (Zn_xO_y, where $x > y$), which give the film its characteristically dark appearance (dark gray to black vs the white of type I films).[12,15]

Similar corrosion reactions are likely to occur in more complex solutions such as groundwater. Under such conditions, ZVZ corrosion is expected to be influenced by the presence of anions that can be categorized into three different types: (i) those that increase ZVZ solubility (e.g., Cl^-, SO_4^{2-}), (ii) those that reduce the solubility of ZVZ and thus promote formation of potentially protective zinc salts (e.g., CO_3^{2-}, PO_4^{3-}), and (iii) those that react with the ZVZ surface and potentially form passive films (e.g., CrO_4^{2-}).[12] These solute effects are often concentration dependent,[12] and few corrosion studies have addressed the effects at concentrations relevant to groundwater. This study assesses the effect of solutes, as present in groundwater over a range of pH, on the reactivity of ZVZ toward TCP.

■ EXPERIMENTAL SECTION

Reagents. The ZVZ used in this study included three industrial-grade materials, Zinc Dust 64 and Zinc Powders 1210 and 1239 (Horsehead Corporation, Monaca, PA). Basic material properties of these materials are summarized in the Supporting Information, Table S1. The ZVZ was used as received. Saturated stock solutions of 1,2,3-trichloropropane (>98%, Fluka) were prepared in deionized (Milli-Q) water. In most experiments, deioinized (DI) water was used without further treatment. Deoxygenated, deionized (DO/DI) water was prepared by sparging with either nitrogen or argon for ~1 h. Groundwater samples were obtained from three sites in Washington and California and designated Site Water P, Q, and M (SWP, SWQ, SWM). Relevant background on the composition of these samples is given in the Supporting Information, Table S4. The groundwater samples were used as received, unless otherwise specified. Artificial groundwater solutions were prepared in DI water using ACS certified salts.

Batch Experiments. Batch reactor experiments were performed in 160 mL serum vials sealed with Hycar septa (Thermo Scientific) and aluminum crimp caps. Reactors were filled with 20 g ZVZ and 80 mL of DI water, deoxygenated DI water (DO/DI water), groundwater, or artificial groundwater. Before addition of TCP, the ZVZ and solution were "pre-exposed" at room temperature for 20−28 h while rotating end-over-end at ~9 rpm. pH values other than approximately 8.5−10 were obtained by titration with HCl or NaOH (buffers were not used to avoid complications from buffer-metal interactions). Titration induced changes to ionic strength and chloride concentration were not expected to have a significant impact on ZVZ

reactivity (more information on ionic strength effects can be found in the Supporting Information, Figure S2, and the effect of Cl^- addition can be seen in Figure 4). When pH was adjusted, the titration was performed approximately one hour into the pre-exposure period in order to first allow initial pH of the ZVZ/water system to stabilize (measurements of pH change over time showed that the pH of DI water increased rapidly to about 8.5−10 upon the addition of ZVZ (Zn64), but reached a steady value by about 15 min, results not shown). After the pre-exposure period, experiments were initiated by injection of 200 μL saturated aqueous TCP stock solution (for $[TCP]_0 \approx 30~\mu M$) and then rotated end-over-end at ~32 rpm for the duration. The "initial" batch reactor pH was measured after the pre-exposure period, just prior to TCP addition. "Final" batch reactor pH was measured at experiment termination.

Analysis. Aliquots (1 mL) were removed from the batch reactor and analyzed by gas chromatography (GC) with a DB-624 column (J&W/Agilent) and electron capture detection. GC analysis was either performed by headspace analysis of the 1 mL aliquot in a 20 mL headspace vial or by direct injection of a 1:1 hexane extraction of the aliquot. TCP concentrations were determined through comparison to calibration curves prepared by analyzing batch reactors containing various concentrations of TCP in DI water. All batch reactors (including those used in calibration) contained a 1:1 ratio of liquid to headspace. Although this ratio varied slightly between experiments (due to volume occupied by the ZVZ) and during experiments (due to the removal of aliquots for analysis), partitioning calculations indicate that the percent of TCP present in the aqueous and vapor volumes of the batch reactors was fairly constant in all cases (98−99% in the aqueous phase).

Data Fitting and Normalization. Concentration versus time data were fit to pseudo-first-order kinetics to obtain observed rate constants (k_{obs}). In some cases, these data were either normalized to the mass concentration of ZVZ in the batch reactor to obtain mass-normalized rate constants (k_M) or to the surface area concentration (using the specific surface areas obtained by BET N_2-gas adsorption) to obtain surface-area-normalized rate constants (k_{SA}). The surface area values used for this are given in the Supporting Information, Table S1.

Characterization. ZVZ was characterized as received and after ~24 h exposure to either DI water or groundwater, at pH 6.8, ~9.7, and 11.9. Those exposed to solution were separated by vacuum filtration in an inert atmosphere. Filtrates were rinsed three times with acetone and vacuum-dried. Characterizations performed on the dry particles included transmission electron microscopy (TEM) with energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD). Details of methods for these analyses are provided in the Supporting Information (Section 4).

■ RESULTS AND DISCUSSION

Use of Industrial-Grade ZVZ. The practicality of using ZVZ for treatment of TCP-contaminated groundwater requires the availability of significant quantities of low-cost, sufficiently reactive material. In a recent study,[11] we evaluated the most readily available industrial-grade granular scrap ZVZ, screening for reactivity in both batch reactors and columns. The results, which are summarized as Supporting Information (Figure S1), show that these materials display similar reactivity to the reagent-grade ZVZ we evaluated previously.[4] One of these industrial-grade
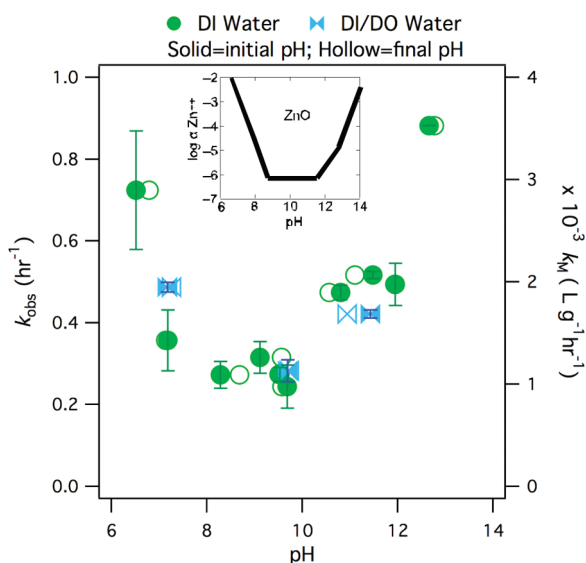
Figure 1. Observed reaction rate constants (k_{obs}) and corresponding mass-normalized reaction rate constants (k_M) versus pH for reduction of TCP by 250 g/L Zn64 in DI and DI/DO water. The rate constant for each experiment is plotted versus the initial and final pH of the batch reactor (shown with solid and hollow symbols, respectively). The resulting pair of points represents the range of pH relevant to each experiment. Error bars shown are ± one standard deviation around the k_{obs} fit to the raw concentration versus time data. Inset: Solubility diagram for ZnO in DI water (shown in more detail in the Supporting Information, Figure S6A).

materials, Zinc Dust 64 (Zn64), showed somewhat higher reactivity on a mass-normalized basis, and the rates of TCP degradation were relatively unaffected by dissolved oxygen (Supporting Information, Figure S1). In addition, Zn64 was confirmed to produce propene as the main TCP dechlorination product (shown in the Supporting Information, Figure S3). These considerations led us to select Zn64 for the evaluation of solution chemistry effects presented here.

Effect of pH in DI Water. The reactivity of ZVZ toward TCP in DI water was found to be highly pH dependent. As seen in Figure 1, a 3-fold variation was observed in the rate constants for TCP disappearance in the presence of Zn64 over the pH range of 6.51 to 12.7. This degree of variation is similar to that observed for ZVI degradation of carbon tetrachloride over a pH range of 5–10,[17] although the "U"-shaped trend is unique. Minimum reactivity was observed from approximately pH 8–10. At pH values outside of this range, reactivity increased under increasingly acidic or basic conditions. This trend parallels the pH dependence of both ZVZ corrosion rate[14] and ZnO/Zn(OH)$_2$ solubility[13] in DI water. These trends show minima at pH 12 (for corrosion rate) and pH 9 (for solubility) with increased corrosion or solubility at higher and lower pH. The shape and minimum of the trend displayed in Figure 1 most closely resembles the trend for zinc (hydr)oxide solubility (Figure 1, inset), suggesting that solubility related changes to the phase (e.g., dissolution) strongly influence ZVZ reactivity. TEM/EDS, XPS, and XRD analysis of the ZVZ particles exposed to DI water at pH 6.8, 9.6, and 11.9 (shown in the Supporting Information, Section 4) confirm that the surface is primarily coated with ZnO and Zn(OH)$_2$.

Effect of pH in Groundwater. Compared with the effect of pH in DI water, varying the pH of groundwater produced a
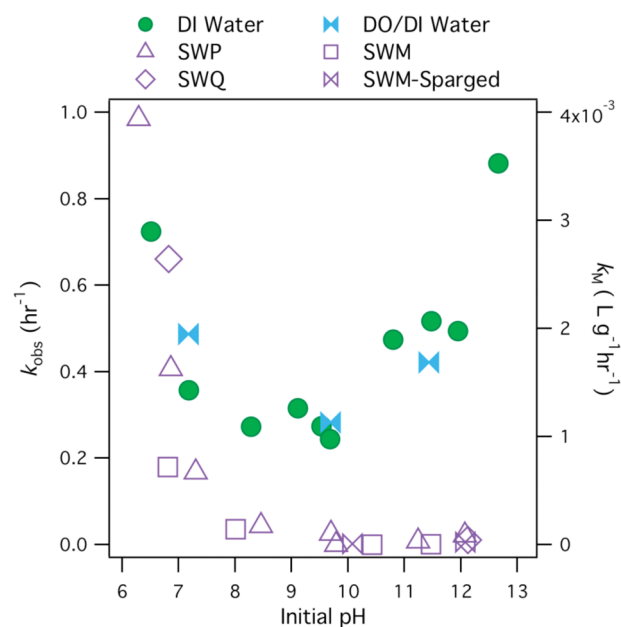

Figure 2. Rate constants (k_{obs} and corresponding values of k_M) for TCP degradation by Zn64 in DI water and groundwater (obtained from sites "P", "Q", and "M") at various pH values. Data for DI water are the same as in Figure 1. Uncertainties in k_{obs} are not shown for clarity, but they are similar to those shown in Figure 1.

distinctly different trend in the rate of TCP degradation. Figure 2 shows the rate constants for TCP degradation in groundwater from pH 6.29 to 12.1; also shown is a simplified version of the DI water data shown in Figure 1 (to facilitate comparison of the trends). At alkaline pH, the rates of TPC degradation are smaller than in DI water. Around pH 10, a typical pH for the system, the k_{obs} measured in groundwater is approximately 1 order of magnitude smaller than that measured in DI water (corresponding to an increase in half-life from 2.57 to 26.7 h). This degree of groundwater inhibition is somewhat larger than is usually observed with ZVI: for example, Liu et al.,[18] observed TCE degradation rates using nZVI to be 3.5–7.5 times slower in groundwater than in DI water. Another notable difference seen in the groundwater data is the absence of the "U"-shaped trend noted in DI water; under these conditions, it appears that increased pH does not result in increased reactivity of ZVZ.

The difference in reactivity of ZVZ in groundwater compared to ZVZ in DI water—as shown in Figure 2—suggests that a factor other than ZnO solubility controls reactivity in groundwater. As mentioned in the introduction, ZVZ corrosion can be influenced by anions that (i) increase ZVZ solubility, (ii) reduce ZVZ solubility and promote formation of potentially protective zinc salts, or (iii) react with the ZVZ surface to potentially form passivating films.[12] The slower kinetics observed in the presence of groundwater solutes at alkaline pH indicate that the system must be affected by one of the scenarios (or some combination) resulting in slower corrosion—and therefore reactivity—of ZVZ, namely, scenario (ii) or (iii). Both of these scenarios involve changes to the ZVZ surface, so it is expected that the surface of ZVZ exposed to groundwater will display different surface characteristics than ZVZ exposed to DI water. The reactivity data suggests there will also be a difference in the surface characteristics of ZVZ particles exposed to acidic and alkaline groundwater (Figure 2). There are then three categories of
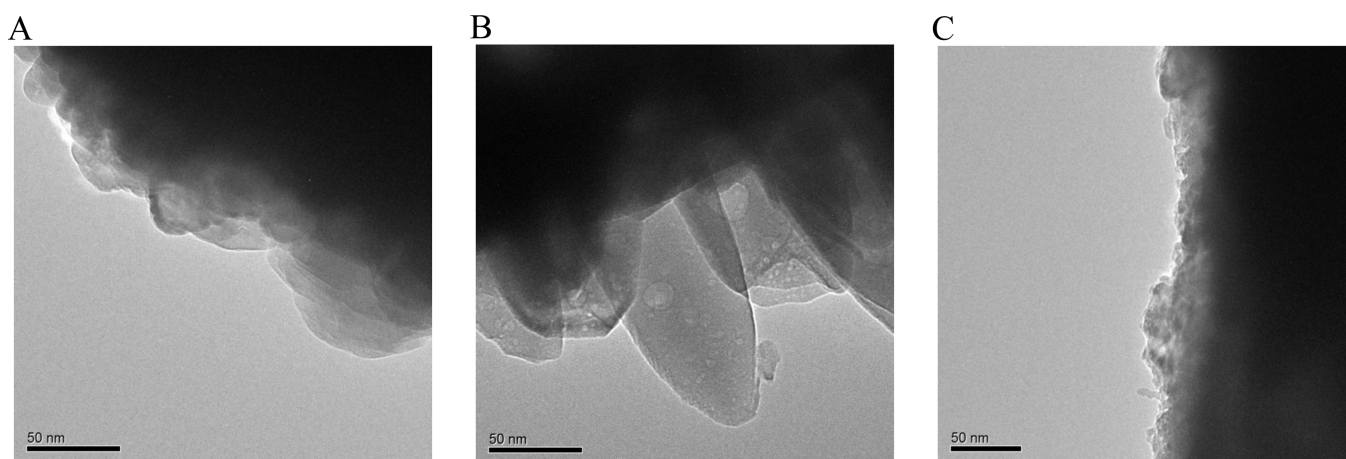
Figure 3. TEM images of ZVZ exposed to (**A**) DI water, displaying a type I film; (**B**) acidic groundwater, displaying a type I film; and (**C**) alkaline groundwater, displaying a type II film. More detail is given in the Supporting Information, Figure S4.

solution-exposed particles, (i) those exposed to DI water, (ii) those exposed to acidic groundwater, (iii) those exposed to alkaline groundwater, all with potentially different surface characteristics, perhaps taking the form of type I (nonpassivating) and type II (passivating) films.

TEMs of ZVZ particles exposed to DI water and groundwater over a range of pH support the presence of morphologically distinct surface films on particles exposed to DI water, acidic groundwater, and alkaline groundwater. On samples exposed to DI water, at all pH values tested, this film is nonuniform and composed of large, round crystallites (a representative TEM image is shown in Figure 3A, the complete set of TEM images is shown in the Supporting Information, Figure S4). On samples exposed to acidic groundwater (SWP), the film is also nonuniform with large crystallites, but the crystallite morphology is more needle-like (Figure 3B). On samples exposed to alkaline groundwater (SWP), the film is more uniform and is composed of compact crystallites (e.g., Figure 3C). The latter film also appears somewhat thinner, an interpretation supported by XRD analysis (Supporting Information, Table S2) showing a lower ZnO content and higher Zn^0 content in samples exposed to alkaline groundwater compared to the other solution-exposed samples. The relative thickness of the oxide layer on the ZVZ particles exposed to DI water and acidic groundwater, combined with the high reactivity of the particles, suggests that the ZnO on the surface is present as a type I film. Such a film would allow for the continued corrosion of ZVZ, thereby supporting the high degradation rates observed in these solutions. The compact film present on ZVZ exposed to alkaline groundwater (pH 9.8 and 11.9), combined with the limited reactivity of these particles, suggests the presence of a thin, passivating type II film. The presence of this film would inhibit further corrosion of ZVZ and limit interaction of ZVZ with the aqueous surroundings resulting in the low degradation rates observed.

Effect of Groundwater Solutes. Despite the insights into the structure of the oxide film gained from the TEMs of ZVZ exposed to DI water and groundwater, these data did not reveal precisely what caused the type II film to form in groundwater. The formation of this film is likely to be due to interactions of ZVZ with anions present in groundwater such as carbonate, phosphate, or silicate, all of which are known to inhibit ZVZ corrosion when their concentrations are sufficient.[12,15,19−24] To

isolate any effects of anions present in our groundwater samples, we performed batch reactor experiments in solutions containing the corrosion inhibitors listed above, and other anions, at or above their concentrations in Site Water P (SWP). We believe SWP to be a representative sample, as most of the constituents were present at concentrations within the ranges that are typical of groundwater.[25−27] The constituents with higher concentrations were Na^+, Cl^-, and SO_4^{2-}, which were included in our tests. The other solutes tested included borate, nitrate, and natural organic mater (NOM) because these are well know to have passivating effects on corrosion of ZVI. The results of all these "artificial groundwater" experiments are shown in Figure 4.

As seen in Figure 4, most of the constituents tested had little effect on the rate of TCP disappearance. The small (±0.1 h^{-1}) deviations from the rates measured in DI water can be attributed to pH and ionic strength effects, as these parameters were not controlled (more information on batch reactor pH and ionic strength can be found in the Supporting Information, Table S4). Even some anions known to strongly inhibit ZVZ corrosion (carbonate, phosphate) did not show a large effect on TCP disappearance rates at the concentration of SWP. Lower disappearance rates were measured when the phosphate concentration was increased by 3 orders of magnitude to 0.2 mM, but this concentration is at least 2 orders of magnitude higher than is typical for groundwater (the median concentration of total phosphorus in groundwater is 20 μg/L (0.65 μM)[26]), so this effect is unlikely to be significant in most groundwaters. The other solutions to produce low disappearance rates contained sodium meta silicate ($Na_2O_3Si \cdot 9H_2O$) prepared at concentrations of 0.45 mM and 0.89 mM. The measured concentration of silica (as SiO_2) in SWP is 0.45 mM. The concentrations of these silicate solutions, which were approximately equal to 26 and 53 ppm SiO_2(aq), are within the typical groundwater range of 5−85 ppm.[26]

Inhibition by Si has been observed previously in studies utilizing ZVI as the reductant. In these studies, SiO_2 was seen to inhibit the reduction of a number or organohalides[28−30] and nitroaromatic compounds[30] by adsorption to the ZVI surface. While the reactivity of ZVZ with contaminants in silicate solutions has not, to our knowledge, been previously investigated, many studies have addressed the effect of silicate anions on ZVZ corrosion.[12,15,19−24] These studies show that ZVZ corrosion
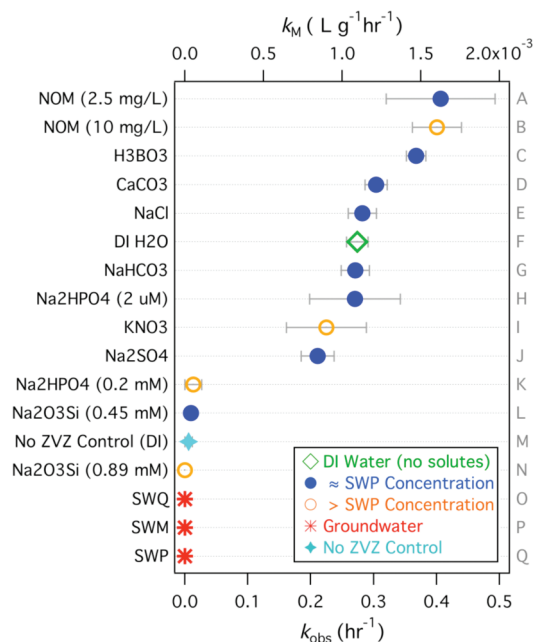
Figure 4. Rate constants (k_{obs} and corresponding k_M) for TCP reduction by Zn64 in various solutions, including DI water, groundwater (SWQ, SWP, and SWM), and artificial groundwater prepared at, or above, the reported concentration for Site Water P. pH and ionic strength were not controlled. Error bars shown are $\pm$ one standard deviation around k_{obs} from the fit to concentration versus time data. Detailed documentation of experimental conditions, listed according to the letters shown on the right of the figure, is given in the Supporting Information, Table S4.

(or reactivity) is decreased in the presence of silicate, and they attribute the inhibitory effect of silicate to incorporation of Si into or onto the surface of the ZVZ in a Zn-rich conversion layer. This incorporation likely occurs through adsorption of silicate anions [15,21,22] and/or the formation of zinc silicate films.[15,20] In the first case, silicate anions outcompete hydroxide for active sites on the ZVZ (due to stronger adsorption).[15] In the second case, the zinc silicate film presumably passivates the ZVZ surface by forming a physical barrier limiting metal-solvent interactions. Geochemical speciation modeling (shown in the Supporting Information, Section 6) predicts $ZnSiO_4$ to be the thermodynamically favorable solid phase under the solute conditions of SWP (vs ZnO in DI water), supporting the second case.

However, surface analysis did not give evidence for a zinc silicate film on the surface of ZVZ exposed to groundwater (nor other typical passive film forming zinc salts such as $ZnCO_3$). Rather, the data (XPS, XRD, etc.) suggest that the films on these particles were primarily composed of ZnO and $Zn(OH)_2$ (Supporting Information, Section 4), suggesting that the first case, silicate anion adsorption, was responsible for the observed inhibition. It is possible that, in the case of alkaline groundwater, a lack of interaction with hydroxide caused by adsorption of silicate anions led to the formation of the observed type II film. XPS of ZVZ exposed to DI water and groundwater at pH 6.8, ~9.7, and 11.9 showed slightly elevated levels of silicon on ZVZ exposed to alkaline groundwater (atomic concentrations of 0.77−1.18% vs 0.21−0.42%). These samples also showed slightly elevated levels of magnesium and calcium, suggesting that these ions may also play a role in the formation of the passive film. Regardless of the
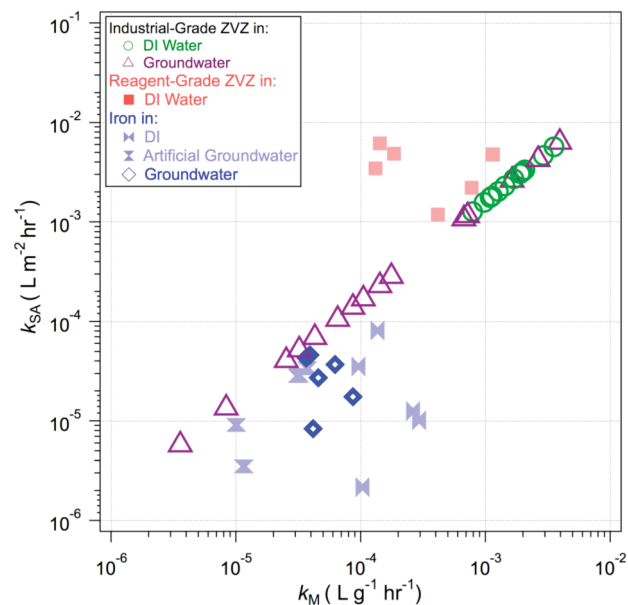

Figure 5. $k_{SA}-k_M$ plot showing TCP degradation rates using Zn64 in DI water and groundwater (as reported in Figure 2) superimposed onto previously collected data using reagent-grade ZVZ in DI water and various ZVI materials in DI water and artificial groundwater. The Zn64 data fall along a line, the slope of which corresponds to the specific surface area (m^2 g^{-1}) of the material. New data for ZVI reduction of TCP in groundwater are also shown. Previously reported data are shown in faded, solid symbols and new data are shown in bold, hollow symbols.

exact mechanism of the inhibited reactivity of ZVZ toward TCP in groundwater, the effect is likely to be prevalent because the necessary components are common constituents of groundwater.

Implications for Groundwater Remediation. In order to put the ZVZ data from this study into context with previously measured data, we compared our new ZVZ data, collected under relatively realistic groundwater treatment conditions, with previously reported data, which included ZVZ data collected with reagent-grade material in DI water and ZVI data collected with various grades of materials under a variety of conditions.[4] The resulting values are plotted in Figure 5 (using the log k_{SA} versus log k_M format that we have described previously [31]). Figure 5 shows data reported previously[4] in faded, solid symbols and new data in bold, hollow symbols. The industrial-grade ZVZ data collected in DI water and groundwater are the same as those shown in Figure 2 (note that they represent a range of pH). It can be seen that, while all the new ZVZ data collected in DI water clusters with the previously measured reagent-grade ZVZ values, the ZVZ data gathered in groundwater over a pH range of about 6−13 spans a much wider range of reactivity. The inhibited TCP degradation kinetics observed with ZVZ in alkaline groundwater display similar k_M and k_{SA} values to those obtained with ZVI.

Given the perspective provided by Figure 5, it is unclear whether ZVZ or ZVI will be more effective in field treatment. It appears that only if groundwater inhibition can be overcome through optimization of the treatment system (e.g., buffering the system at acidic pH, pretreating groundwater to remove inhibiting constituents, or pretreating the ZVZ to protect it from passivation), will the potential reactivity advantages of ZVZ be achievable in the field. Alternatively, it is possible that degradation kinetics will not be the most important factor in determining the overall performance of ZVZ in the various configurations that

it might be used in field-scale remediation of TCP. Other considerations have barely been investigated, such as the possibility of permeability losses due to hydrogen-bubble formation, changes in reactivity over the long-term due to particle coating and pore blockage by secondary precipitates, hydrogeological factors that might extend the size of the dissolved Zn^{2+} plume beyond from the zone of treatment, and the cost to performance trade-offs of diluting ZVZ with other granular materials.

■ ASSOCIATED CONTENT

Ⓢ　Supporting Information.　Details on the properties and reactivity of ZVZ, the effect of ionic strength on TCP reduction by ZVZ, the products of TCP degradation, the preparation and properties of the artificial groundwater solutions, the methods and detailed results of particle characterization, as well as geochemical speciation modeling for ZVZ in solution. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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