DEGRADATION AND DECONTAMINATION OF VX IN CONCRETE

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Reactions of VX in concrete have been studied in situ using solid state ^{31}P NMR. The size of VX drops deposited on concrete affect the natural degradation rate, with 4 µL drops reacting faster than 0.2 µL drops. Water added to concrete samples containing sorbed VX to mimic precipitation and/or a potential decontamination strategy resulted in the desorption of copious amounts of VX into the water along with its decomposition products. The rate of VX degradation in the presence of external water was only slightly enhanced relative to the background degradation rate. Decontamination of VX sorbed in concrete using the new Decon Green^{TM} decontaminant resulted in the nearly complete reaction of VX within a few hours.

INTRODUCTION

The importance of drop sizes and their environmental persistence arises from the predicted size range of VX droplets reaching the ground following a military chemical attack, 0.01 to 2 µL,[1] and the need for battlefield commanders to know the severity and endurance of the hazard. Decisions must be made whether to expend time and resources performing wide-area decontamination or to determine if natural weathering, alone, will allow resumption of normal operations after an acceptable waiting period. Indeed, if wide-area decontamination is warranted for a known persistent agent such as VX, proper decontamination procedures need to be developed and employed to successfully remediate the hazard.

Recent studies examining the persistence of VX in concrete have produced seemingly widely different results. Examining both small, neat 0.01-µL VX drops and solvent-assisted submonolayer applications of VX, Groenwold et al.,[2] found that VX did not persist on concrete beyaond a day or so. Yet in our preliminary study,[3] using the exact same concrete as Groenwold et al.,[2] large drops of VX on the order of several µL's persisted for more than a month. It was observed, however, that a small fraction of the applied VX did react relatively quickly within a few hours. This fraction of VX reacting quickly corresponded to about 1 monolayer, evidence that concrete does possess a reactive capacity of about 1 monolayer for VX. Therefore, the idea of a reactive concrete surface with a capacity limited to about 1 monolayer for VX that becomes overwhelmed by large droplets reconciles our result with those of Groenwold et al.[2]

VX undergoes a slow, but selective hydrolysis in water to yield nontoxic ethyl methylphosphonate (EMPA) as shown in Scheme 1.[4] On the other hand, basic hydrolysis is nonselective, yielding up to 22% of the toxic *S*-[2-(diisopropylamino)ethyl] methyl-phosphono thioate (EA-2192).[5] In our preliminary study[3] we noted that VX degradation on the aged concrete was selective for EMPA, as EA-2192 was not detected by ^{31}P NMR. Using IT-SIMS, Groenwold et al.[2] also did not detect any EA-2192 formation on concrete.

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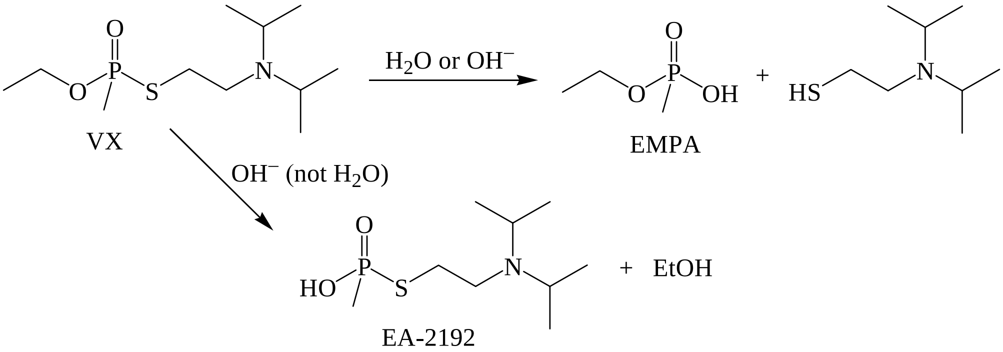
SCHEME 1



In the current study, the persistence of various drop sizes of VX is examined on fresh concrete and these results are compared to those of the preliminary study.[3] Additionally, the effect of two potential wide-area decontaminants, water and the new Decon Green™ decontaminant[6] are examined.

RESULTS AND DISCUSSION

^{31}P NMR spectra obtained for VX drops of sizes 4, 2, 1, 0.5, and 0.2 µL applied to 8 mm × 2 mm × 15 mm fresh concrete coupons are shown in Figure 1. Note that varying the number of drops kept the total amount of VX at 4 µL for each sample. The fresh concrete was 2 months old when this experiment was conducted. The spectra yield overlapping peaks for VX (63 ppm) and EMPA (28 ppm), and lines have been added to the spectra to aid the reader in discerning these peaks. It is observed that in all cases VX slowly decomposes to EMPA over the course of several days; however, the smaller drops react considerably faster than the large drops. After 4 days, considerable VX remains for the 4-µL drop sample; a small amount of residual VX is evident as a shoulder for the 2-µL drop sample; but no residual VX is apparent for the 1 µL and smaller drop samples. The effect of using a solvent (hexane) to uniformly spread the same amount of VX (4 µL) across the concrete surface was investigated. This experiment was conducted after the "fresh" concrete had aged 14 months, so a control experiment using a single 4-µL drop of VX was also examined. As with the smaller drops above, the hexane-spread VX sample reacted considerably faster than the single 4-µL drop sample, with the former reacting within 5 days in contrast to 9 days for the latter.

In contrast to the previous study where VX persisted on an aged concrete sample for months, VX only persists for days on the fresh concrete. Moreover, the exceptional reactivity of the "fresh" concrete was maintained for at least 14 months. The pH measured for water containing crushed samples of the concretes was about 10 for the fresh concrete (after 14 months ageing) and 9 for the aged concrete. Thus the higher pH of the fresh concrete is one apparent factor for it's increased reactivity. Also, ^{31}P NMR suggests increased mobility for the VX sorbed on the fresh concrete owing to its much narrower NMR line; another contributing factor to the enhanced reactivity.

Additional experiments examining the effect of decontamination attempts using water and the new Decon Green™ decontaminant were conducted. With 1 mL water added to VX sorbed on the fresh concrete, VX was immediately desorbed from the concrete and persisted beyond three days. Thus the addition of water did not significantly enhance the degradation rate of VX. Indeed, water-induced desorption of VX from concrete may actually increase its contact and/or vapor hazard. Besides VX, the decomposition products EMPA and EA-2192 were also desorbed by water and detected; however, the latter toxic compound did not persist, slowly reacting to non-toxic methylphosphonic acid (MPA) over the course of a few weeks. In contrast to water, addition of 0.8 mL Decon Green™ resulted in the complete reaction of VX within a few hours and did not significantly desorb VX. Moreover, formation of toxic EA-2192 was avoided owing to the selective nature of the VX reaction with Decon Green™.[10]

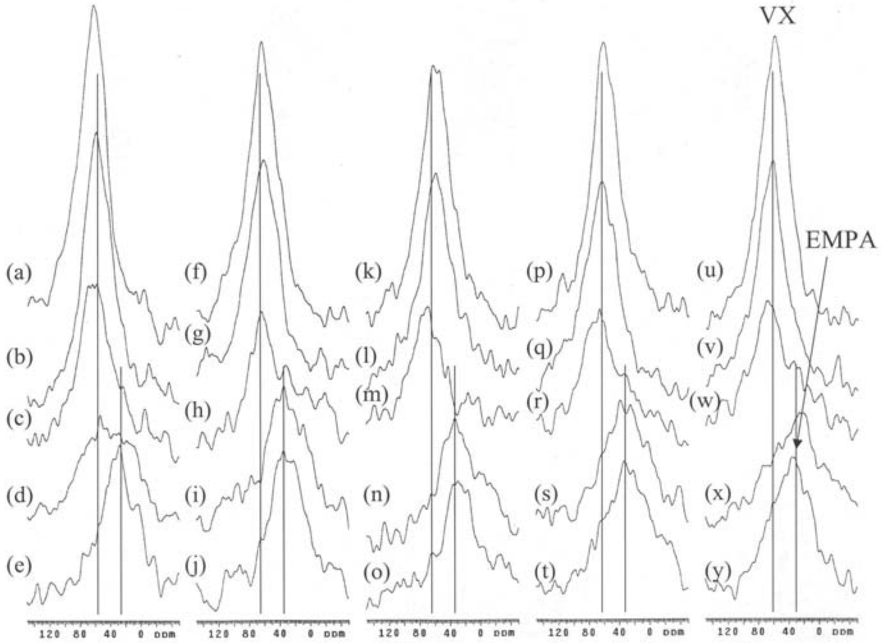


FIGURE 1. Selected ^{31}P NMR spectra obtained for VX added to concrete coupons at (top to bottom) 1 h, 5 h, 29 h, 4 days and 11days: one-4 μL drop (a-e); two-2 μL drops (f-j); four-1 μL drops (k-o), eight-0.5 μL drops (p-t) and twenty-0.2 μL drops (u-y).

CONCLUSION

VX degrades significantly faster on fresh concrete than on aged concrete. Contributing factors include the higher pH and increased mobility of VX on fresh concrete. There is a marked drop size effect for the degradation of VX on concrete, with sub-μL sized droplets reacting significantly faster than larger drops. Decontamination with water leads to desorption of VX and its products – potentially increasing the VX contact/vapor hazard – but does not significantly enhance the rate of degradation. In stark contrast, decontamination with Decon Green^{TM} affords the complete reaction of VX within a few hours, and does not significantly desorb VX.

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