

Decay Kinetics of Peroxyacetic Acid (PAA) and Hydrogen Peroxide (PERASAN ®, EPA #63838-2) in a Variety of Water Matrices

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I. Introduction

In order for peroxyacetic acid (PAA) to be approved by the U.S. EPA for treatment of municipal wastewater, certain data that the agency has requested must be submitted by the registrant. The ecological impact of PAA forms part of this data package. In particular, the U.S. EPA has requested testing the aquatic toxicity of PAA to a variety of fish, shrimp, algae, and plant life. This ecological data will also be used in support of local NPDES permitting.

It is known that the decay kinetics of PAA in water is a strong function of the particular water matrix to which it has been introduced. Factors influencing the stability of PAA in an aqueous system include pH, ionic strength, salinity, temperature, and the presence of transition metal ions etc.. This study reports on the comparative stability of PAA (and hydrogen peroxide) when different water matrices were dosed to high and low levels of PAA that are likely to be employed in the practical treatment of municipal wastewater effluent. The objective is to define the baseline stability condition of PAA in water matrices to be employed in the subsequent aquatic toxicity tests. Clearly, the baseline stability condition will represent the maximum stability that PAA would be expected to exhibit. In the actual toxicity-testing program where PAA is introduced to a variety of aquatic lifeforms, the persistency of PAA may be considerably lower than the baseline stability condition. This is because PAA is a reactive chemical, and is depleted when it reacts with microorganisms or the higher lifeforms. Indeed, PAA functions as a biocide by this mechanism.

II. Executive Summary

The decay kinetics of peracetic acid and hydrogen peroxide in a variety of different aqueous matrices has been defined. Measurements were conducted over a 96-hour reaction time at minimum and maximum doses of product. The goal was to define the baseline stability condition of PAA and hydrogen peroxide in water matrices that are to be employed in subsequent aquatic toxicity tests. It was found that the rate of PAA depletion was a function of both the water matrix and the applied dose. At high concentration, the half-life of PAA in seawater is only 12 minutes, but is around 24-30 hours in ordinary water depending upon the calcium hardness. At low concentration, the half-life of PAA in seawater is 30 minutes, and is estimated to be around 8-17 hours in ordinary water of moderate and high hardness, respectively. Hydrogen peroxide has far greater chemical stability than PAA in all the aqueous matrices tested. At both high and low doses of PAA, there was negligible decay of hydrogen peroxide throughout the 96-hour monitoring period.

III. Conclusions

- The rate of PAA depletion is a function of the both the water matrix and the applied dose of product introduced to the water.
- In seawater, the half-life of PAA is estimated to be 30 minutes at the low dose (1 ppm PAA), and 12 minutes at the high dose (20 ppm PAA).
- In water of moderate hardness, the half-life of PAA is estimated to be 7-8 hours at the low dose (1 ppm PAA), and around 30 hours at the high dose (20 ppm PAA).
- In water high hardness, the half-life of PAA is estimated to be 17-18 hours at the low dose (1 ppm PAA), and around 30 hours at the high dose (20 ppm PAA).
- Hydrogen peroxide has far greater chemical stability than PAA in all the aqueous matrices tested. At both high and low doses of PAA, there was negligible decay of hydrogen peroxide throughout the 96-hour monitoring period.

IV. Experimental

Three different source waters were selected to be dosed with a low level of 1 ppm PAA, and a high level of 20 ppm PAA. These were 1) moderately hard EPA reconstituted water commonly used for chronic toxicity testing of freshwater organisms; 2) very hard EPA reconstituted water; 3) seawater made from 35 parts per thousand sea salt (Instant Ocean supplied by Aquarium Systems, Mentor, OH) dissolved in de-ionized water.

Table 1 summarizes the pH, conductivity, total alkalinity, and total hardness that was measured for each source of water.

Table 1

	pH	Conductivity µmho/cm	Total alkalinity/ ppm as CaCO ₃	Total hardness/ ppm as CaCO ₃
Moderately hard EPA water	7.7	341	60	74
Very hard EPA water	7.98	1280	240	300
Seawater	7.9	45000	240	6400

The decay profiles of the PAA (and H₂O₂) dosed solutions were monitored for 96 hours as this is the length of time over which the aquatic toxicity testing is to be conducted. However, all analytical measurements for PAA were terminated when its concentration approached the detection limit of the analytical procedure employed.

V. Determination of Peracetic Acid (PAA) and Hydrogen Peroxide (H₂O₂) In Water

Introduction

This analytical technique employs a color indicator (DPD) that turns pink in response to the presence of PAA. A colorimeter programmed to measure the intensity of the pink coloration and display the result in terms of ppm as Cl₂ is also used. A simple calculation is then used to convert this number into the ppm as PAA. Hydrogen peroxide does not interfere with the measurement for PAA. In order for the hydrogen peroxide to be measured, it must be activated by addition of a catalyst and then given time to react. Upon addition of the DPD indicator, the intensity of the pink coloration measured by the colorimeter is now the sum of the PAA and hydrogen peroxide concentrations expressed as ppm Cl₂. After subtracting the contribution due to PAA, a simple calculation is then used to convert this number into ppm as H₂O₂.

Equipment and Reagents

Chlorine – Pocket Colorimeter. Hach Model 46700-00

DPD TOTAL Chlorine Reagent Powder Pillows for 10 ml sample size. Hach Product number 21056-69. ***Important note:*** Do ***NOT*** use DPD FREE Chlorine Reagent Powder Pillows.

Hydrogen Peroxide Activator 1 (15% KI solution)

Hydrogen Peroxide Activator 2 (4% ammonium molybdate solution)

Procedure for PAA

Before testing, make sure the instrument is in the low (LO) range mode by checking that the display reads to hundredths (0.00)

Note: the sample must be analyzed immediately; it cannot be preserved for subsequent analysis.

- (1) Fill both 10 ml sample cells with the water sample. Designate one of these to be the blank and one to be the prepared sample.
- (2) Add the contents of one DPD TOTAL Chlorine powder pillow to the prepared sample cell.

- (3) Cap the prepared sample cell and shake gently to mix the DPD powder. A pink color will develop indicating the presence of PAA.
- (4) Within 30 seconds of adding the DPD powder to the prepared sample cell, cap the blank cell and place it in the cell holder with the diamond mark facing you. Cover the cell compartment with the instrument cap to shield from stray light interferences and then press ZERO.
- (5) The instrument will turn on and the display will show --- then 0.00. Remove the blank cell and replace it with the prepared sample cell. Align the cell and cover the cell compartment and then press READ.
- (6) The instrument display will show --- followed by the results in ppm total chlorine. This is the ppm total Cl₂ PAA value

Calculation

$$\text{ppm PAA} = 1.07 \times \text{ppm total Cl}_2 \text{ PAA}$$

Procedure for Hydrogen Peroxide

Before testing, make sure the instrument is in the low (LO) range mode by checking that the display reads to hundredths (0.00)

Note: the sample must be analyzed immediately; it cannot be preserved for subsequent analysis.

- (1) Fill both 10 ml sample cells with the water sample. Designate one of these to be the blank and one to be the prepared sample.
- (2) Add 3 drops of Hydrogen Peroxide Activator 1 and 3 drops of Hydrogen Peroxide Activator 2 to the prepared sample cell.
- (3) Swirl the prepared sample cell to mix and let react for 6 minutes.
- (4) Then, add the contents of one DPD TOTAL Chlorine powder pillow.
- (5) Cap the prepared sample cell and shake gently to mix the DPD powder. A pink color will develop.
- (6) Within 30 seconds of adding the DPD powder to the prepared sample cell, cap the blank cell and place it in the cell holder with the diamond mark facing you. Cover the cell compartment with the instrument cap to shield from stray light interferences and then press ZERO.
- (7) The instrument will turn on and the display will show --- then 0.00. Remove the blank cell and replace it with the prepared sample cell. Align the cell and cover the cell compartment and then press READ.
- (8) The instrument display will show --- followed by the results in ppm total chlorine. This is the total Cl₂ peroxygen value.

Calculation

$$\text{ppm H}_2\text{O}_2 = 0.478 \times (\text{total Cl}_2 \text{ peroxygen} - \text{total Cl}_2 \text{ PAA})$$

V. Results & Discussion

The decay profile monitoring was performed in a laboratory under ambient temperature conditions (19-22 °C) throughout the 96-hour test period. Samples were stored in opaque HDPE bottles fitted with screw caps to guard against any photochemical or evaporative interferences. The results are report in Figures 1-6 of Appendix A

It soon became apparent, that for PAA at least, the decay profile could be segregated into 2 distinct regions; one at short reaction times (minutes) and the other throughout the entire reaction period (hours). These were graphed at both the low (1 ppm PAA) and high (20 ppm) concentration ranges. By contrast, the hydrogen peroxide did not exhibit such dramatic matrix effects, and therefore was only plotted over the entire reaction period for both high and low dosage ranges.

Figure 1 of Appendix A charts the short-term decay profile for the low PAA dose (1 ppm). It is striking that the PAA is almost totally depleted within 4 hours of its introduction to seawater. By contrast, PAA is relatively stable in EPA reconstituted water of moderate and high hardness.

Figure 2 of Appendix A represents the long-term decay profile of PAA at the lower nominal dose. The instability of PAA in seawater is again exemplified. The decay of PAA is slower in high hardness water than it is in moderately hard water. This enhanced stability might be due to the ability of PAA to form a 5-membered chelation ring around a calcium ion co-ordination center. Nevertheless, it is apparent that in all 3 water matrices, the amount of PAA remaining in solution approaches the 0.05 ppm detection limit of the analytical procedure well before the 96-hour monitoring period is complete.

Figure 3 of Appendix A plots the high concentration of PAA (20 ppm) at short contact times. Again, PAA is most unstable in seawater, and is completely depleted within 2 hours. The decay of PAA in EPA reconstituted water of moderate and high hardness is much slower, and relatively little is depleted within the first 4 hours.

Figure 4 of Appendix A charts the long-term decay profile of PAA at the higher nominal dose of 20 ppm. The decay of PAA in moderately hard and very hard EPA reconstituted water track each other for about 48 hours after which the very hard water experiences an unexpected rapid decline. This is most likely due to the presence of some contaminant being inadvertently introduced to the bottle upon sampling.

Figures 5 and 6 of Appendix A plot the extended term decay profiles of low and high doses of hydrogen peroxide in the different aqueous matrices. It is immediately apparent that hydrogen peroxide is far more stable than PAA in all the aqueous matrices employed in this study. In fact, even in seawater there is negligible depletion over the 96 hour reaction time. The fluctuation that is observed is within the experimental reproducibility of the analytical technique.

An estimate of the reaction half-life of PAA was made from the decay profiles by judging the time elapsed for one half of the initial concentration to be depleted. Table 2 reports the half-life data estimated from the decay profiles of Figures 1-4.

Table 2

	Half life of PAA	
	Low Dose (1 ppm)	High Dose (20 ppm)
Seawater	30 minutes	12 minutes
Moderately hard EPA water	7-8 hours	30 hours
Very hard EPA water	17-18 hours	30 hours

The half-life of hydrogen peroxide was not estimated since insufficient decay had occurred over the 96-hour reaction time to permit an accurate assessment.

Appendix A
Figures 1-6

Figure 1: Short Term Decay Profile of PAA

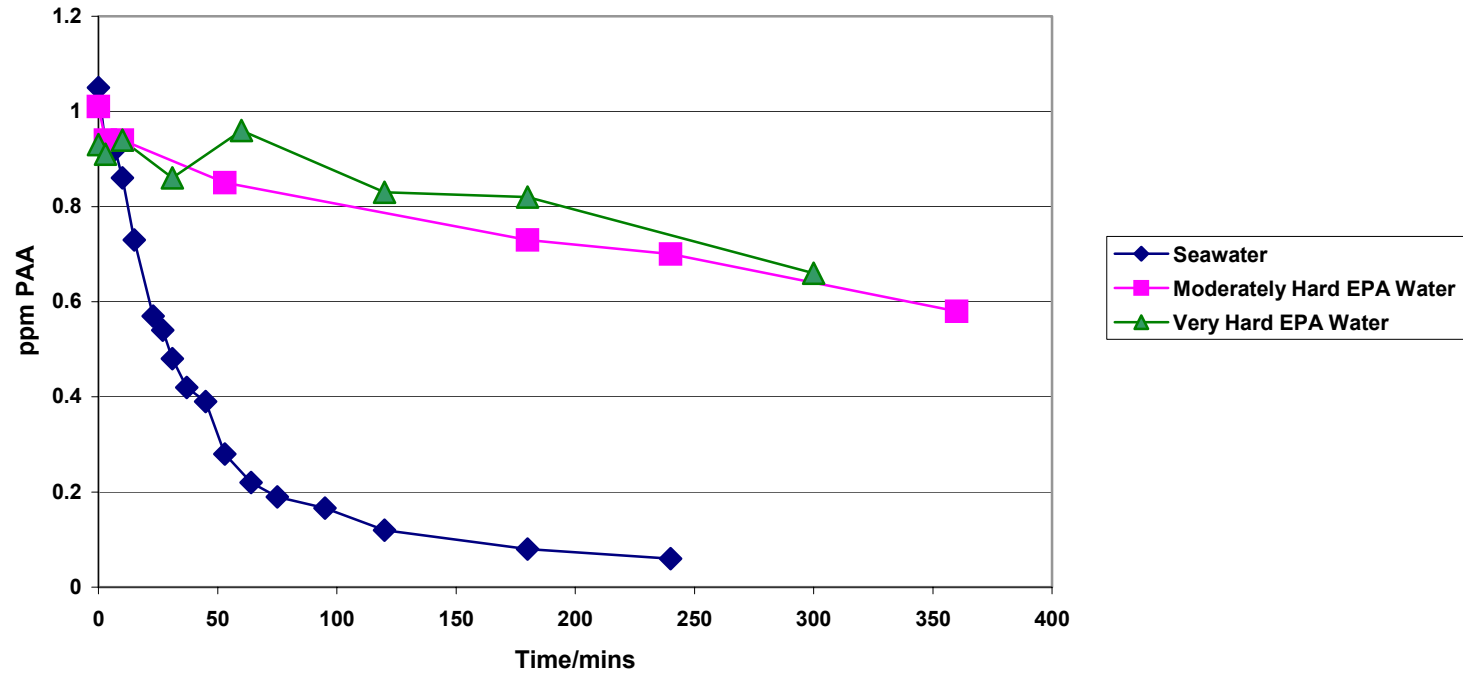


Figure 2: Long Term Decay Profile of PAA

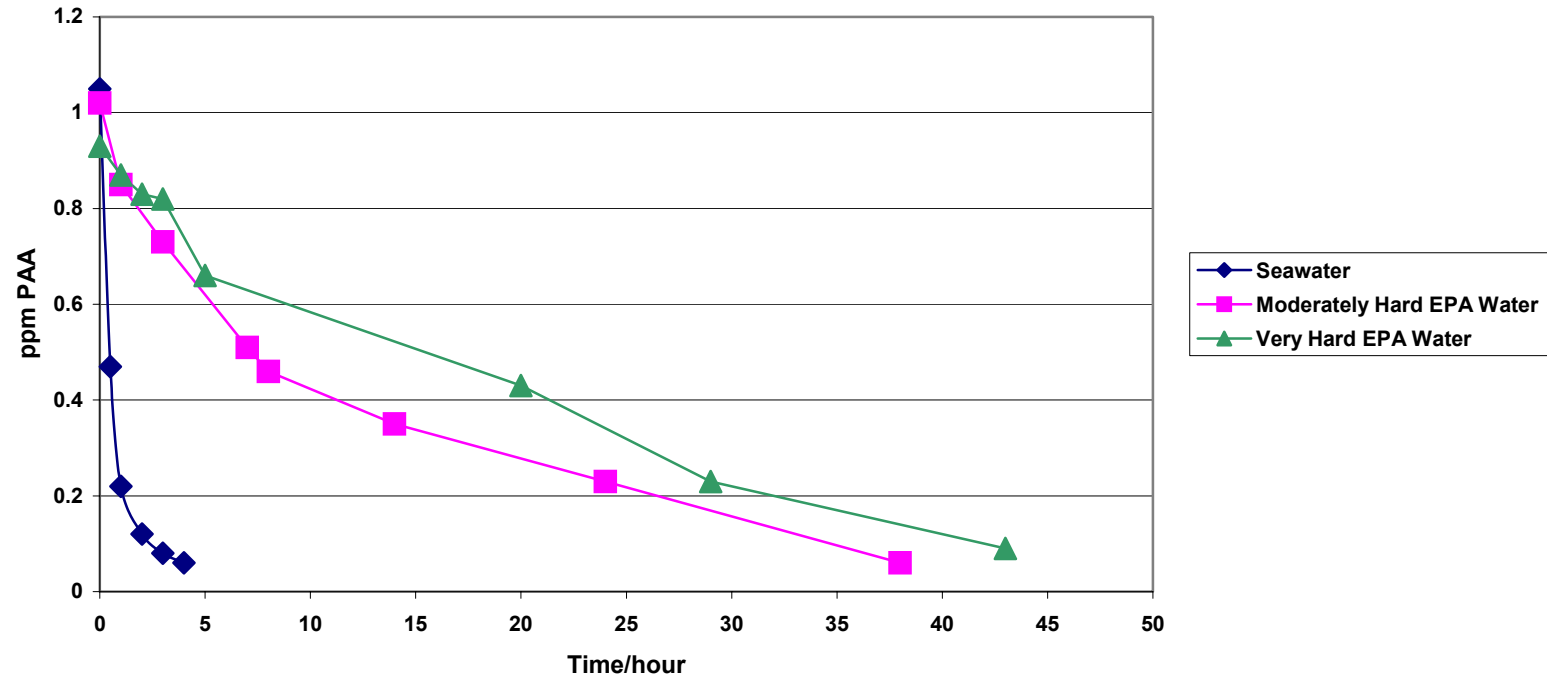


Figure 3: Short Term Decay Profile of PAA

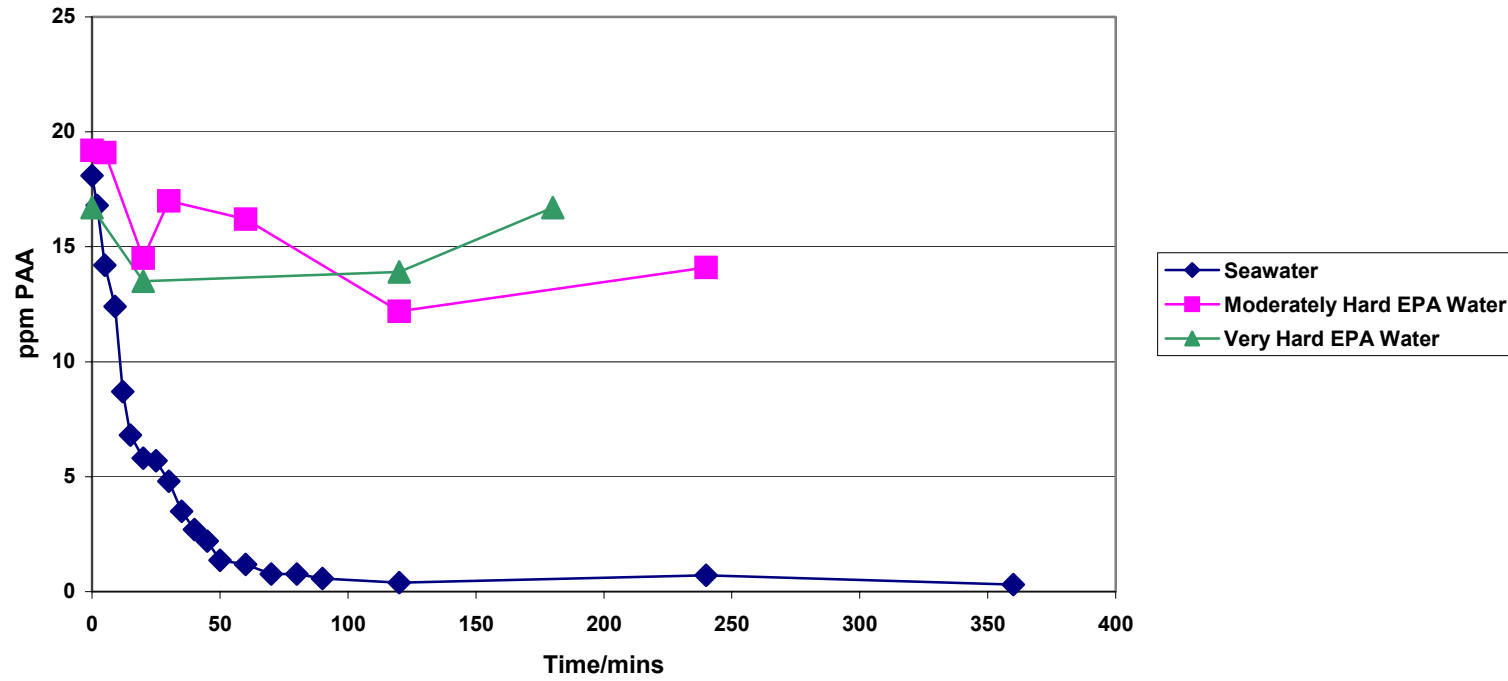


Figure 4: Long Term PAA Decay Profile

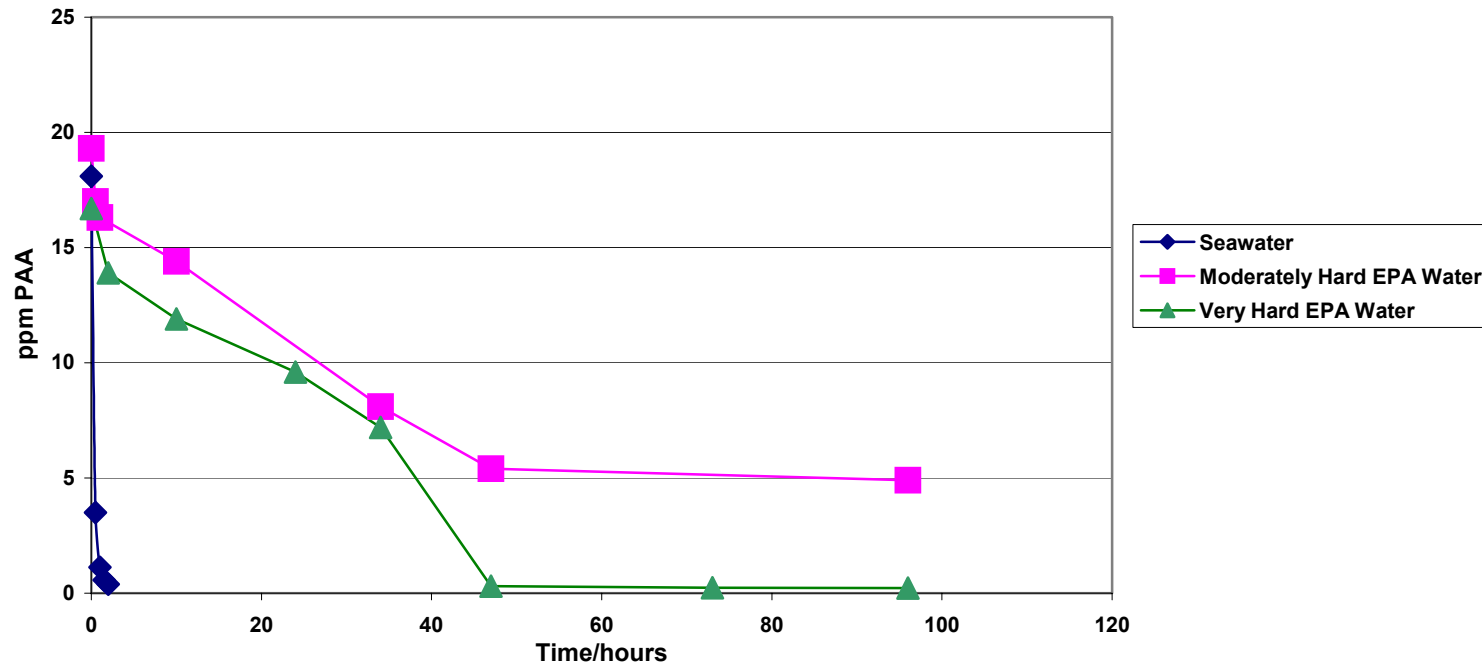


Figure 5: Long Term Decay Profile of Hydrogen Peroxide

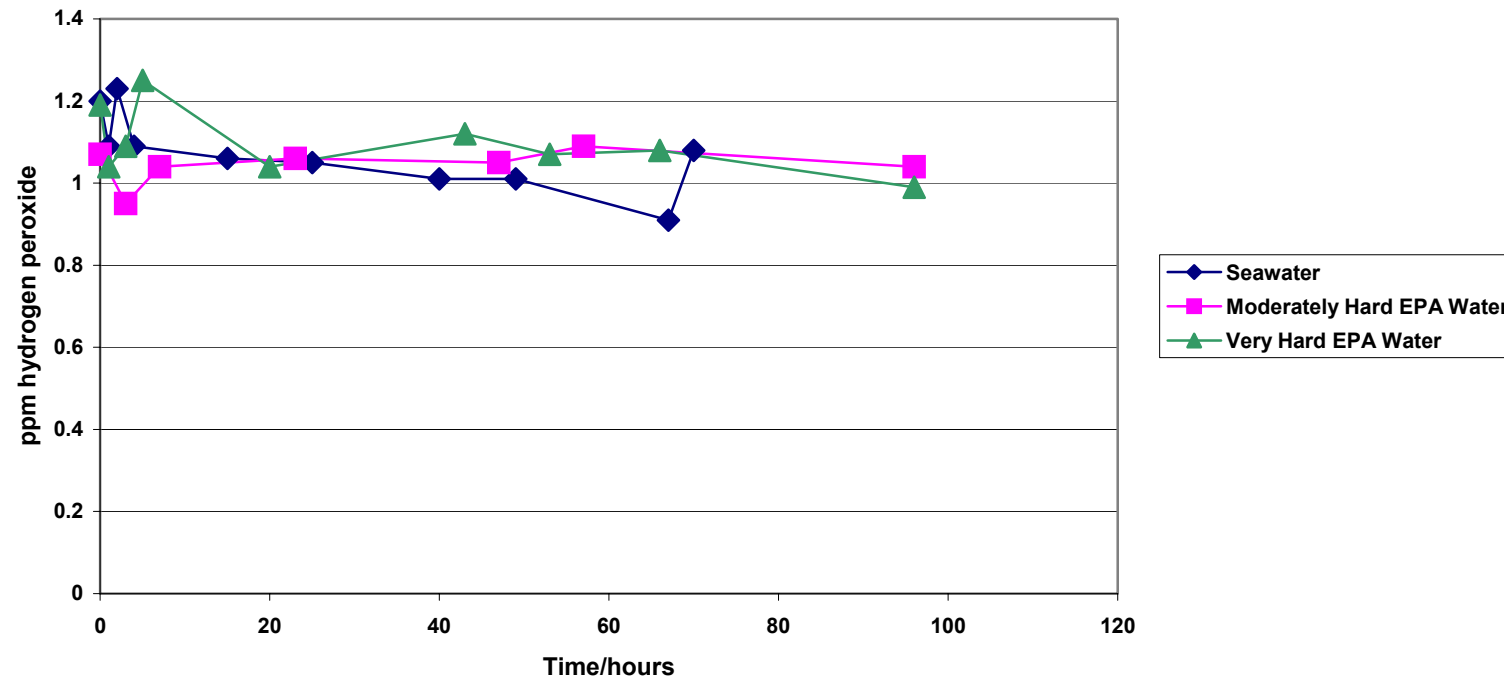


Figure 6: Long Term Decay Profile of Hydrogen Peroxide

