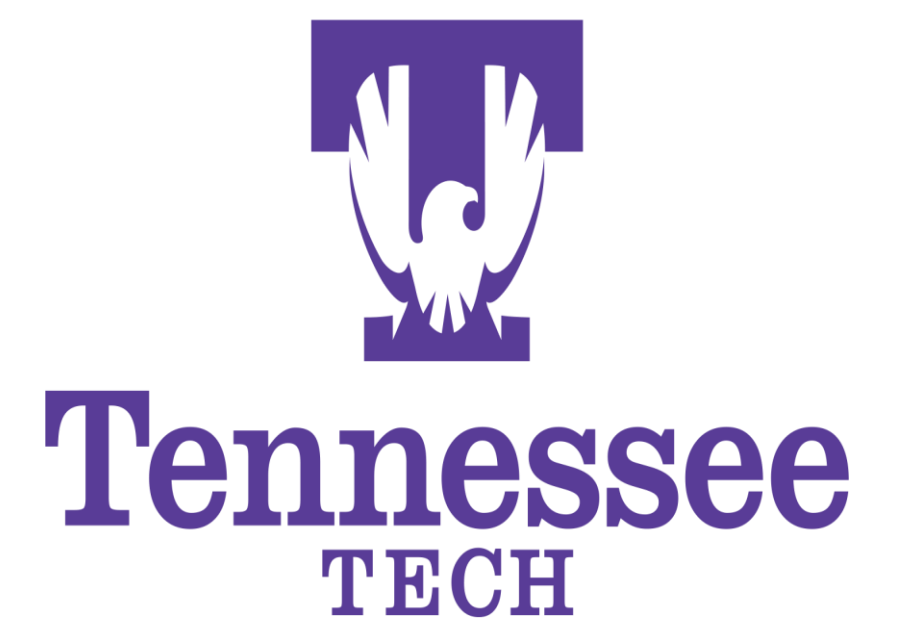


A study on the spectrophotometric analysis of Hg(II) using dithizone under conditions pertinent to Hg(II) reduction in aquatic systems

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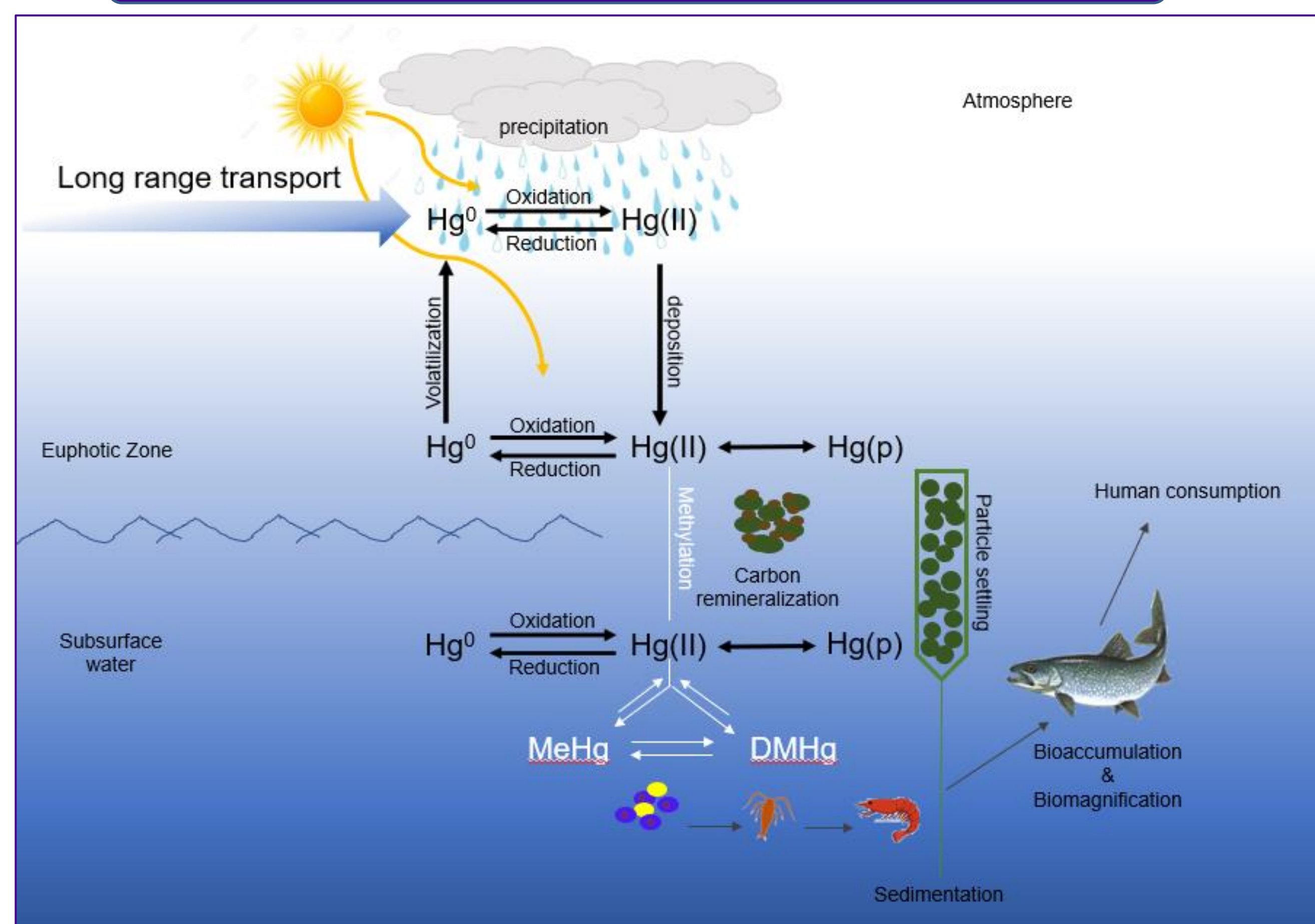
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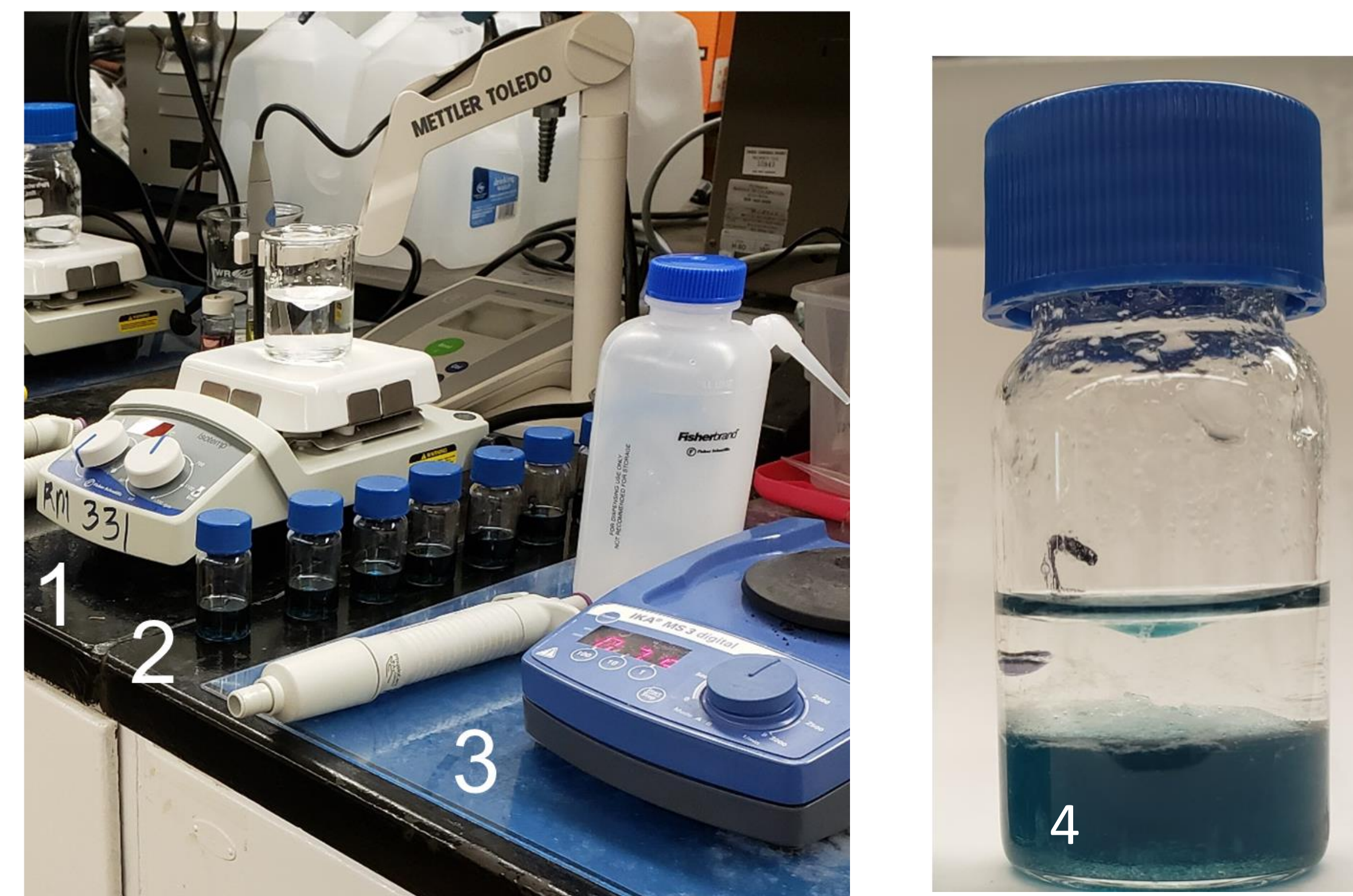
Introduction

- Atmospheric mercury (Hg) undergoes long range transportation and is deposited to aquatic systems across the globe as Hg(II).
- Hg loss from aquatic systems can occur through Hg(II) photoreduction to aqueous Hg⁰.
- Photoreduction decreases the amount of Hg(II) available for methylation to the more toxic Hg species.
- We do not know all reduction pathways for various Hg species in different aquatic ecosystems.
- Identifying Hg(II) reduction pathways is important for estimating the retention of Hg in aquatic systems and the ultimate fate of Hg in the environment.
- We hypothesize that the superoxide free radical is an important Hg(II) reductant and that the dithizone method is suitable for studying this pathway.

Hg Biogeochemical Cycle



Methods



1. Solutions containing Hg complexes (ex. Hg-Citrate) and xanthine were placed on a stir plate and pH adjusted to 7.2. The solution was stirred for 5 minutes before a control was taken to ensure other reduction pathways were not taking place. Xanthine oxidase was then added to start the superoxide production.

$$\text{Superoxide production: xanthine} + \text{O}_2 \rightarrow \text{O}_2^{\cdot -} + \text{uric acid}$$
2. Aliquots of the solution were pipetted into an equal amount of dithizone solution every 4 minutes for 20 minutes.
3. Samples were shaken on a digital shaker.
4. Samples were left still for 10 minutes to ensure the completion formation of the mercury-dithizone complex.
5. The organic phase was transferred to a cuvette for spectrophotometric analysis at 496 nm,

Results

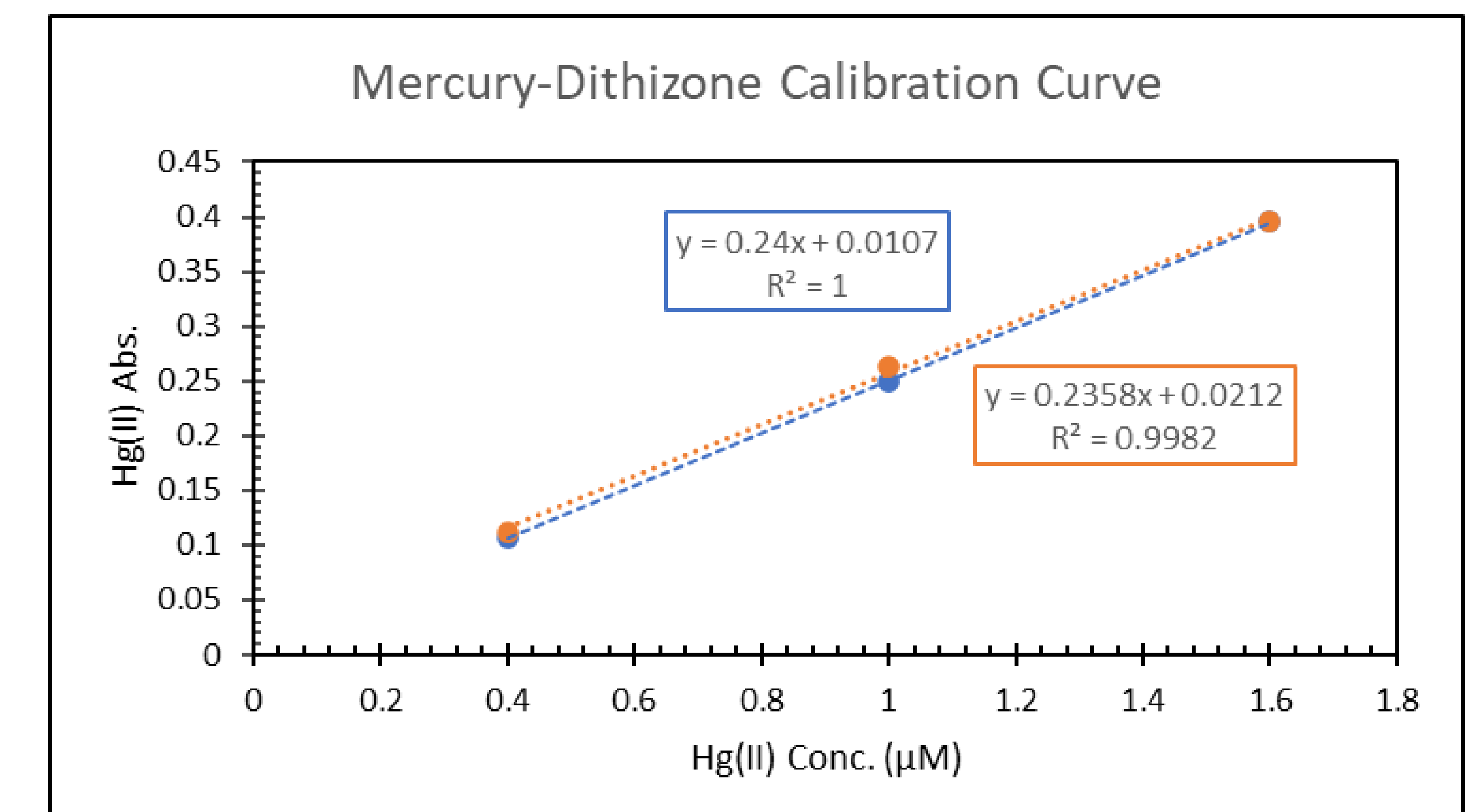


Figure 1. Examples of the calibration curves for spectrophotometric analysis of Hg(II) using dithizone. The blue line represents an aqueous system containing only Hg(II) at pH 3. The orange line represents an aqueous solution containing Hg(II)-citrate in the presence of xanthine at pH 7.2.

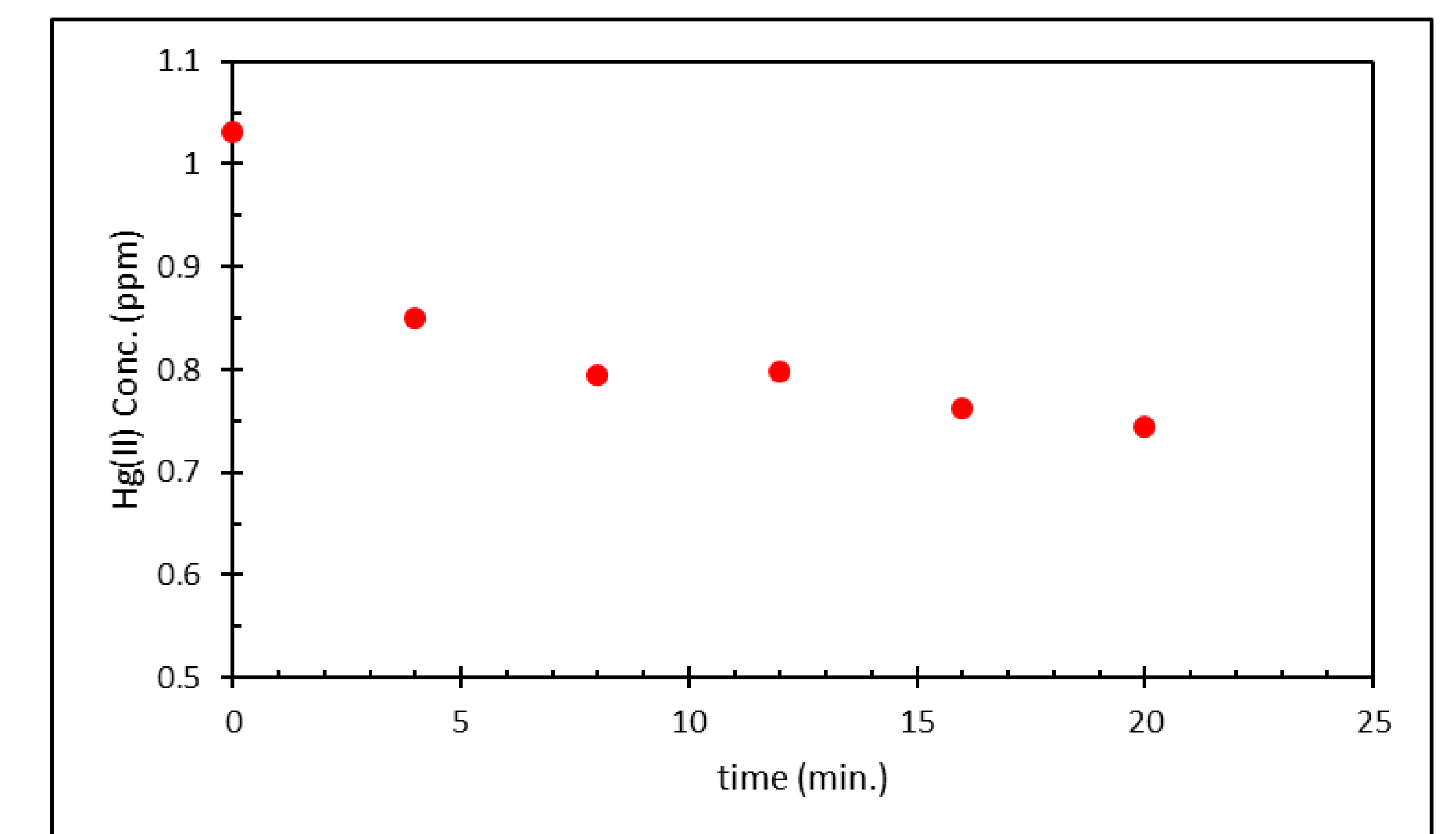


Figure 2. Typical kinetic data from Hg(II) trapping experiments with dithizone when mercury is provided initially at 1 ppm (5 µM) Hg(II) complexed with 0.001 M citrate at pH 7.2. Error bars from triplicate runs are negligible on the graph.

Discussion and Conclusions

- The spectrophotometric analysis of Hg(II) using dithizone appears to be applicable to the conditions pertinent to the study on Hg(II) reduction under the environmental conditions investigated and thus can serve as a useful method for further investigation of Hg(II) reduction pathways.
- Preliminary data indicates that superoxide reduces Hg(II) complexed with citrate by 0.3 ppm in 20 minutes with no UV radiation (photochemistry) applied.
- We hypothesize that the amount of superoxide mediated Hg(II) reduction will increase under UV light.
- An intensive kinetic study is currently underway to understand the role of superoxide on the mercury redox cycle.

Table 1. Hg(II)-Citrate reduction data in the presence of superoxide

| time (min.) | Absorbance at 496 nm | | | | [Hg(II)] (ppm) | Std.Dev. |
|-------------|----------------------|---------|---------|-------|----------------|----------|
| | Trial 1 | Trial 2 | Trial 3 | Mean | | |
| 0 | 0.264 | 0.260 | 0.269 | 0.264 | 1.0311 | 0.004509 |
| 4 | 0.221 | 0.224 | 0.220 | 0.222 | 0.8502 | 0.002082 |
| 8 | 0.210 | 0.206 | 0.210 | 0.209 | 0.7950 | 0.002309 |
| 12 | 0.209 | 0.207 | 0.212 | 0.209 | 0.7979 | 0.002517 |
| 16 | 0.200 | 0.200 | 0.203 | 0.201 | 0.7625 | 0.001732 |
| 20 | 0.200 | 0.192 | 0.198 | 0.197 | 0.7441 | 0.004163 |

Table 1. Hg(II) concentration was calculated from the orange calibration line shown in Fig.1 and using the mean absorbance from triplicate runs: $[\text{Hg(II)}] = (\text{mean Abs.} - 0.0212)/0.2358$.