

# Arsenic concentration and flood discharge in Southern California

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## Abstract

*Arsenic in the environment is a hazard to human and ecosystem health. Understanding how arsenic behaves in nature aids in ecological remediation and prevention of contamination of groundwater sources. Using data published by the Natural Resources Conservation Service (NRCS) and the United States Geological Survey (USGS) StreamStats application, the relationship between arsenic (As) concentration in groundwater and maximum discharge during flood events was examined in Southern California. After normalizing data points to their respective drainage basin area, a negative correlation between arsenic concentration and discharge during flooding events arises. Power regression lines for high arsenic concentration data produce an  $R^2$  value of 0.83, and low arsenic concentration data produce an  $R^2$  value of 0.83—both of which are within acceptable ranges defined in the study.*

## Introduction

The purpose of this paper is to investigate any possible statistical correlations between arsenic concentrations in Southern California with peak flooding discharge for various recurrence intervals. Past research connecting groundwater chemistry and geomorphology has been established, and this article seeks to examine specific variables in order to gather evidence on this connection.<sup>1,2</sup> The expected result was a negative correlation between flood discharge and arsenic concentration—as peak flood discharge increases, arsenic concentrations will decrease. The proposed hypothesis was that more arsenic will be removed from the area by larger flooding events, resulting in a decrease in the observed arsenic concentrations. Essentially, the flooding will ‘wash’ away the arsenic from the area, as one might expect. The null hypothesis was that there is no relation or correlation between arsenic concentration and flood discharge—that is, both are variables which are independent of, and uninfluenced by, each other.

Southern California was chosen as the study site due to the presence of many anthropological sources of arsenic—such as mining and agricultural practices—as well as the severe drought and water-rights issues present in this region of the state.<sup>3</sup> When water resources become scarce and the prioritization of its users becomes a public concern, the introduction and transportation of contaminants such as arsenic can exacerbate an already large problem. In California, the governmental goal for minimum arsenic concentration in drinking water is 0.004  $\mu\text{g/L}$ —and this limit is strictly enforced by the California Safe Drinking Water Act in order to protect

the state’s residents.<sup>3</sup> Thus, understanding how contaminants behave and how they are influenced by variables such as flooding becomes crucial in ensuring the delivery of clean, safe water to where it is needed.

Arsenic is a highly toxic and carcinogenic substance, and poses a serious hazard not only to human health, but also to ecosystems due to its ability to remain in organisms for extended periods of time.<sup>4</sup> Although high concentrations of As in surface or groundwater is often attributed to anthropogenic practices such as mining operations and the use of agricultural pesticides, arsenic can also be the result of natural weathering processes.<sup>5</sup> The primary concern for human populations is the presence of arsenic in drinking water: An estimated 100 million people consume water containing arsenic above the World Health Organization’s recommended limit of 10 micrograms per liter.<sup>5</sup> Arsenic can be present in solid and aqueous phases as well as several oxidation states; since it is more mobile in its aqueous phase, the presence of arsenic in the aqueous phase is of more concern with respect to the contamination of water sources.<sup>5</sup>

In surface and near surface conditions, two oxidation states of arsenic are most abundant: arsenic (V) and arsenic (III).<sup>5</sup> The ability of arsenic to adsorb onto the surface of soil solids is strongly controlled by its oxidation state. As(V) binds strongly to a wide range of mineral components of soils and sediments and is generally insoluble, whereas As(III) solid phase adsorption is more dependent on certain soil chemical conditions (see Table 1).<sup>5</sup>

Solid state arsenic in minerals can be broken down into two categories: arsenates, which contain the  $\text{AsO}_4^{3-}$  anion; and arsenites,

which are less common, and contain the  $\text{AsO}_3^{3-}$  anion.<sup>6</sup> Arsenates are associated with arsenic acid ( $\text{H}_3\text{AsO}_4$ ), which has three steps of dissociation.<sup>2</sup>

Additionally, arsenious acid—associated with arsenites—has only one dissolution step, where  $\text{pK} = 9.2$ .<sup>2</sup> The large  $\text{pK}$  value for arsenious acid, as well as steps one and two of the dissociation of arsenic acid, indicates a large reduction in the strength of the acid. Although acidity can be an issue in certain situations, these  $\text{pK}$  values likely mean that just the presence of arsenic in a given environment is more of a concern than the effects of the acids.

There are additional arsenic minerals outside of the arsenates and arsenites that can have an influential presence in a watershed. In areas rich with sulfide minerals (e.g., many mining districts), minerals such as realgar ( $\text{AsS}$ ), orpiment ( $\text{As}_2\text{S}_3$ ), and arsenopyrite ( $\text{FeAsS}$ ) can form. When these minerals are subjected to chemical weathering, arsenic can be produced.<sup>6</sup> Additionally, arsenopyrite can be a byproduct of gold, silver, copper, and lead ore processing, called smelting. The mishandling of this arsenic bearing mineral post-smelting can also result in the release of arsenic into the environment.

Estimates predict as much as half of the arsenic in nature is bound to solid phases, such as soils. In Southeast Asia, sedimentary basins with high concentrations of arsenic in groundwater undergo extended periods of anaerobic conditions; these environmental factors promote the production of highly mobile As(III), compared to As(V)—which is more commonly found in aerobic conditions.<sup>4</sup> A remediation technique in West Bengal involves the process of pumping aerated water to a target depth to create an oxidation zone.<sup>5</sup> This zone promotes the

Adsorbent	As(V) (mmole/Kg)	pH	As(III) (mmole/Kg)	pH
<i>Al Oxides</i>				
Gibbsite	35	4.0		
Amorphous Al hydroxide	15	9.0		
	1500	4.0		
	600	9.0		
	1600	5.0		
	1200	7.0		
	500	9.0		
Activated Al	67	6-7	14	6.5-8.5
Bauxite	52	6-7	16	6.5-8.5
<i>Aluminosilicates</i>				
Montmorillonite	8	5.0	3	5.0
Kaolinite	7	5.0	1	5.0
<i>Fe (hydr)oxides</i>				
Hydrous ferric oxide	3514	4.0	2675	8.0
Goethite				
Magnetite	173	4.0	173	8.0
2-line ferrihydrite			332	8.0
	2000	4.6	>6000	4.6
2-line ferrihydrite on quartz sand	1500	9.2	>6000	9.2
	483	7.1	1206	7.1
<i>Others</i>				
Birnessite	100			
Pyrolusite	10	6.5		
Cryptomelane	25	6.5		
Activated Carbon	10	3-4		
Humic Acids	90-110	5.5		5.5

Table 1. Retention maxima for arsenic on common soil forming minerals<sup>5</sup>

growth of arsenic oxidizing bacteria, which produces the insoluble arsenic (V); the entire process can be carried out in-situ, and does not produce any waste stream.<sup>5</sup>

Concentrations of arsenic are controlled by both climate and geology.<sup>7</sup> Iron oxide bearing minerals appear to release a significant amount of arsenic, and are the most common source of arsenic in areas with high arsenic concentrations.<sup>7</sup> The release of arsenic from iron oxides can be the result of geochemical processes, such as the reaction of iron oxides with organic carbons and hydrocarbons, from either a natural or anthropogenic source.<sup>5</sup> This poses an increased threat from arsenic in areas with large hydrocarbon deposits, and surficial concentrations of arsenic can be exacerbated by events such as oil spills.<sup>5</sup>

Another large source of arsenic in natural settings is from iron oxides in felsic volcanic rocks.<sup>7</sup> When these iron oxides come into contact with alkaline ground water, arsenic undergoes a redox reaction, allowing it to become much more mobile in an aqueous phase.<sup>7</sup> Interestingly enough, a process called iron oxide adsorption is used to remove arsenic from drinking water.<sup>5</sup> The process uses iron hydroxide, which is a strong adsorbent of arsenic—particularly arsenic (V)—at low pH ranges, allowing the purification of the water. In addition to iron oxides, sulfide minerals can be a

source and sink for arsenic.<sup>5</sup> Typically, there is a correlation between areas with high arsenic concentrations in ground water and areas with high evaporation rates, which is very common in the American West and Southwest.<sup>4</sup>

## Methods

Using the USGS StreamStats online application for the state of California, peak flood discharge in liters per second was collected for recurrence intervals of 2, 5, 10, 25, 50, 100, and 500 years, with their associated standard errors in percent. This was completed using the drainage basin delineation from a point tool, which uses calculations, methods, and standards laid out by Thomas et al in the USGS Open-File Report 93-419.<sup>8</sup> The 500 year recurrence interval was not used in the data analysis due to its lack of a standard error statistic, and its anomalously high and infrequent flow parameter. StreamStats was also used to calculate the drainage basin area for each point. Soil composition was found using the NRCS Web Soil Survey online application, which is a compilation of data from various soil survey manuscripts published by the NRCS for California. Care was taken to ensure both points from the Web Soil Survey and StreamStats coincided, and represented the same sample. This was done using various landmarks in each application, such as roads, channels, elevation benchmarks, and USGS gauging stations.

Arsenic concentrations were divided into two populations: high arsenic concentrations ( $\geq 25 \mu\text{g/L}$ ) and low arsenic concentrations ( $< 1.0 \mu\text{g/L}$ ), as defined by Anning et al and Beisner et al.<sup>1,4</sup> Intermediate concentrations of arsenic were omitted—only the highest and lowest brackets of arsenic concentration were used, so that any relationship between flooding and concentrations would become inflated and more apparent. General areas of high and low arsenic concentrations

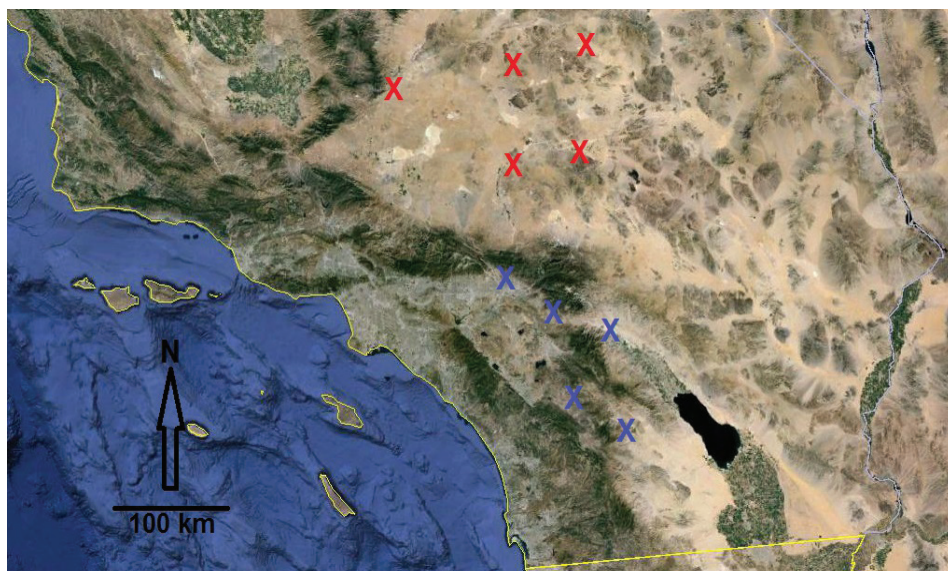


Figure 1. Map showing sampled locations. Red points indicate high arsenic concentration sites, while blue represents low concentration sites.

were determined using data from Besiner et al.<sup>4</sup> These two populations represent the two end members of a range of measured arsenic concentrations collected by Anning et al.<sup>1</sup> For each population, five points were chosen across Southern California (Figure 1), taking care that none were within the same local drainage basin in order to ensure comprehensive and non-overlapping data. Large areas of approximately homogenous arsenic concentrations were common, so chosen points were taken from different areas to ensure a more diverse sampling. To make certain none of the data would become skewed due to arsenic's adsorption behaviors, soil textures of each site were considered. The drainage basin area of each point was used to normalize the peak flood discharges for each recurrence interval, in order to standardize the effects that drainage area could have on arsenic concentration and/or flood discharge.

Acceptable  $R^2$  values for the support of the hypothesis were defined to be  $\geq 0.80$ . That is to say, 80% or more of the correlation can be described using the variables of arsenic concentration and flood discharge. Values for  $R^2$  were calculated using a power regression line for high arsenic concentration data and low arsenic concentration data plotted against flood discharge. Acceptable standard errors were defined as  $\leq 5\%$  of the measured value. Data were entered into and normalized to basin area using Microsoft Excel. Both data sets (normalized and un-normalized) were plotted, and  $R^2$  values were also calculated using Excel. A power regression line was used to find the trend line for each data set (high and low arsenic concentrations), and the  $R^2$  values were calculated using this regression. A logarithmic scale was used for the flood discharge (y) axis to better present the data.

## Data and results

Prior to normalization (see Appendix), plots of flood discharge versus recurrence interval showed a higher discharge rate for the points with high arsenic concentrations ( $R^2=0.685$ ) compared with the points with low arsenic concentrations ( $R^2=0.728$ ). After normalizing each point to its respective drainage basin area (Figure 2), a higher discharge rate per basin unit area was found in the lower arsenic concentration points ( $R^2=0.885$ ) than the higher concentration points ( $R^2=0.834$ ). Both sets of data (high and low concentration points) were comprised of primarily loams (sandy loam, sandy clay loam, etc.) and sands (loamy sand, gravelly loamy sand, etc.), and showed no obvious correlation between soil texture and the other parameters of the points (drainage basin area, flood discharge, and arsenic

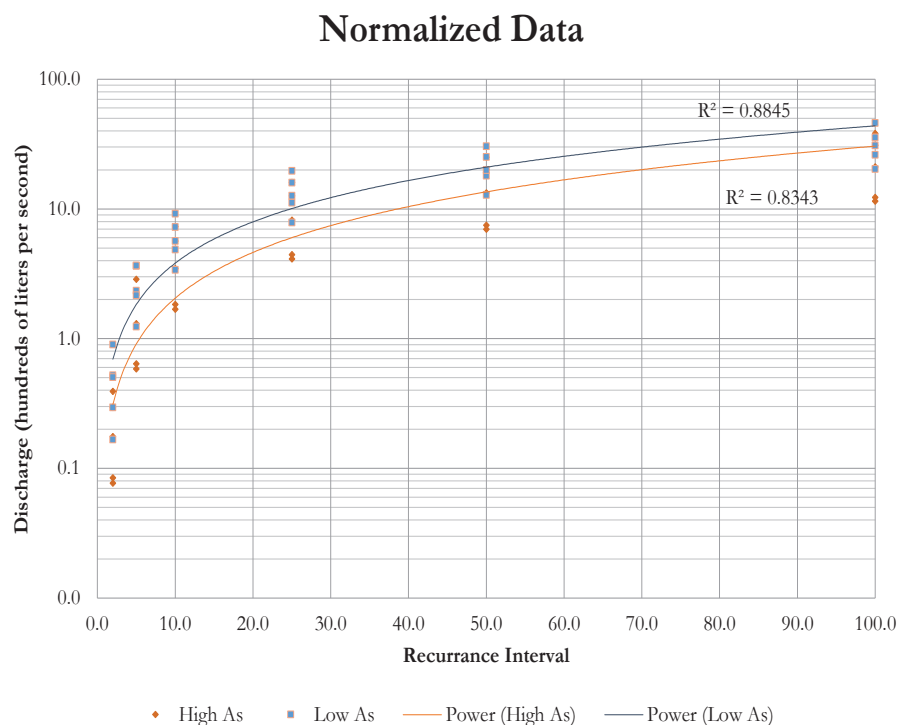


Figure 2. Flood discharge data normalized to basin area. Un-normalized data can be found in the appendix.

concentration). Standard errors were mostly within acceptable ranges (0.6% to 1.2%), except for points six and nine, both of which were low arsenic concentration points and had standard error ranges from 85% to 150%. However, when these points were removed, the  $R^2$  value dropped from 0.885 to 0.877. This was within a reasonable range from the inclusive  $R^2$  value (0.885), and was still distinct enough from the un-normalized  $R^2$  value of 0.728 for these two points to be included in the analysis. When these standard errors were plotted for each point, the range of errors was approximately the same size as the points used to represent the data, so it was discarded. The  $R^2$  values showed that most ( $\geq 80\%$ ) of the controlling variables were included in the analysis.

## Discussion

The statistical evidence strongly supports the hypothesis that there is a negative correlation between arsenic concentrations and peak flood discharge, and that the null hypothesis should be rejected. Of the samples taken, the points with lower arsenic concentrations display larger peak flood discharges; this can be said when the discharge per basin area is considered. The  $R^2$  value is within an acceptable range, indicating that the two variables, peak discharge and arsenic concentration, are

correlated. Since it appears that the arsenic is removed by flooding, it can be assumed that the arsenic removed must have been in an aqueous phase and is readably mobile; both of these conditions point to the preferential removal of As (III) over As (V).

The increase in  $R^2$  values for the normalized data indicate that the basin size is an important variable in the comparison of flood discharge and recurrence interval, presumably because basin area is a control on the cross-sectional area of the flow, which accounts for two of the three variables in the continuity equation. The points with low arsenic concentrations show much higher values for peak flood discharge per basin unit area, indicating a negative correlation between arsenic concentration and flood discharge per basin unit area. The high  $R^2$  values for each set of data points show that many of the controlling variables have been accounted for in the analysis and are high enough to be deemed acceptable, yet not high enough to raise suspicion of both variables representing the same thing.

Based on qualitative descriptions of the soil textures sampled for this study, and with the use of a soil texture ternary diagram, a more quantitative description can be obtained. All soil samples fall into one of the following five soil types: sand, loamy sand, sandy loam, sandy clay loam, and loam (Figure 3). It can be inferred that the soil



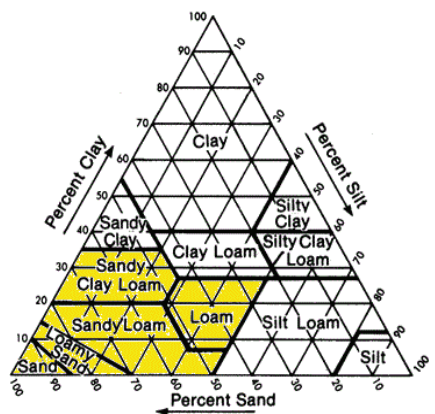


Figure 3. Soil texture ternary diagram, with observed soil textures highlighted<sup>2</sup>

samples all had the following ranges of sand, clay, and silt particle percentages:

*Sand:* 25% to 100%

*Clay:* 0% to 75%

*Silt:* 0% to 50%

With such a wide range of soil textures for both high and low arsenic points, it appears that there is no control on the arsenic concentration from the soil texture. To definitively determine this, however, sample sites containing more silt- and clay-rich soils should be considered in possible future research.

Potential issues arise when other controlling factors on the mobility of arsenic are included. The oxidation state of arsenic can be heavily influenced by environmental factors. If an area contains reducing fluids in contact with arsenic or potential arsenic sinks, arsenic (V) would become more prevalent. Since As (V) is much less resistant and is more likely to become adsorbed by solid phases, flooding would have little influence over the arsenic concentrations in a basin. The exception to this, however, lies in whether or not the sediment, which has As (V) adsorbed to its surfaces, is transported by the flooding event.

Other possible influencing factors must be considered: the capacity and competence of the flooding event, and the proportion of arsenic bearing solid phases in the dissolved, suspended, and bed loads of the flood. Furthermore, the properties of solid phase arsenic and its transportation by the flooding event also need to be included in a more holistic understanding of the correlation. The ability for As (III) to be adsorbed to the solid phase is dependent on the mineral and chemical composition of the solids. Although it is safe to assume that As (V) is the most abundant adsorbed state of arsenic, this cannot be verified until chemical properties of the soil are considered, not just

its textural component.

One other crucial key to determining the controlling variables on arsenic concentrations would be the source of the dissolved or aqueous arsenic. Assuming only As (III) is present in the system due to its relative mobility, groundwater discharge and surface runoff should be examined more closely. Assuming an initial, discrete input of arsenic onto the surface, arsenic concentrations will decrease with increasing number of runoff events; essentially, surficial arsenic is washed away by runoff. It is estimated that about 7% of total arsenic in a system can be transported by surficial runoff, and of that, 38% goes into solution with the rest adsorbing to the solid sediment phase.<sup>5</sup> This transportation by runoff events would be controlled by not just the permeability of the soil, but also the amount of precipitation a particular basin receives. The presence of rain shadows where one side of a drainage divide receives more precipitation than another would heavily influence this transportation by runoff. As a result, all else being equal, two geographically close points separated by a high drainage divide could display two drastically different arsenic concentration measurements. Another factor related to this would be groundwater discharge. Pre-existing arsenic in groundwater, the arsenic's initial source, the source of the groundwater, and how groundwater is interacting with surficial runoff are all things that would need to be determined for each point under investigation, and considered in the analysis. Means of resolving all these potential influential factors in arsenic concentration would be to include quantitative data on these variables in the analysis and the inclusion of a larger sample size, in order to remove any and all factors which may skew the data.

## Conclusions

Statistically speaking, arsenic concentration and flood discharge are negatively correlated—at least for sandy to loamy textured soils when basin area is included. With  $R^2$  values above 0.80 for both high arsenic concentration and low arsenic concentration sites, there is strong evidence to support the relationship between arsenic concentration and flood discharge. To further promote this correlation, studies should be carried out with more control over possible influential variables on arsenic concentration in the ground water, and with a larger sample size of locations.

Whether or not this correlation deems action to remove the effects of flooding on arsenic is beyond the scope of this study. The possibility of the implementation of a remediation technique is an issue

that should be addressed by authorities such as environmental consulting firms or local government agencies. However, understanding how arsenic interacts with its environment is critical in evaluating and implementing remediation procedures. If arsenic is found in excess of this limit, not only is it in violation of laws such as the California Safe Drinking Water Act, it also puts the health of residents at risk. If such a case occurs, remediation efforts must take place in order to protect citizens—and to determine which technique is most effective, scientists and engineers need to have access to as much information on arsenic as possible.

## References

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Appendix

Raw Data

