

HEAVY METALS IN LAKE NAKURU

INTRODUCTION

PURPOSE

The purpose of this module is to explore the hypothesis that heavy metal contamination is responsible for the flamingo deaths at Lake Nakuru. Water chemistry of the lake will be considered as it pertains to the respective chemical state, concentration, sampling and sample preparation of toxic metals found there. In the next section, relevant methods of analysis for these metals will be investigated.

LEARNING OUTCOMES

At the end of this assignment students will be able to:

1. Understand the rudiments of stabilization of water samples.
2. Know the definition of water alkalinity and be able to calculate total alkalinity.
3. Distinguish between soluble and particulate bound metals and understand Langmuir adsorption behavior.

INTRODUCTION

You have already read that toxic trace metals are a possible culprit for the deaths of 40,000 lesser flamingos at Lake Nakuru, Kenya during the time periods of August – November 1993 and August – September 1995. (*Nelson 1998*) Local industries such as tanneries, electroplating facilities, textile mills, battery factories, and paint packaging are the most likely sources of the heavy metals. In this section we further explore this possibility and examine in greater detail the sampling and sample preparation steps that are necessary to evaluate the levels of several candidate metals present in Lake Nakuru water and sediment samples.

The focus of our investigation will be on the metals copper (Cu), zinc (Zn), lead (Pb) and chromium (Cr). Often such metals are referred to as “heavy” or “toxic” metals but, unfortunately, there is not a clear definition of these terms in the scientific literature. (*Duffus, 2002*) The idea that the density of metals may be correlated to their toxicity is not true, and some metals may be required for life at trace levels but toxic at higher levels. To further confuse matters the oxidation state of the metal can be important in determining both its chemical properties and biological effects. For example, for chromium, Cr(III) is much less harmful than Cr(VI).

Three items must be shown to support the hypothesis that heavy metals are responsible for flamingo deaths:

- (1) Demonstration of the identities of heavy metals present in the lake (qualitative analysis) and determination of the concentration levels (quantitative analysis) of each toxic metal present in the lake.
- (2) What is the potential for exposure of the flamingos to each of these metals?

- a. Do the toxic trace metals exist in the lake in forms that will be consumed by the flamingos?
- (3) If exposed, is the dose toxic to the flamingos?

The paper by [Nelson et al. \(1998\)](#) reports the results of a thorough study of heavy metals in water samples taken from Lake Nakuru during 1996. Both water and sediment samples were collected and analyzed by the research team. In addition to evaluating the levels of metal samples in the water samples, adsorption equilibria were studied for the binding of Cu, Zn, Pb and Cr to suspended solids collected from Lake Nakuru and to the algae *S. platensis* grown in pure culture.

Read through the article “Model for Trace Metal Exposure in Filter-Feeding Flamingos at Alkaline Rift Valley Lake, Kenya” (Nelson 1998) and consider the following:

Q1. What is the likely route of exposure (i.e. eating, drinking, or some other means)?

Q2. Why do you think the authors emphasize the importance of particulate bound metals rather than metal ions dissolved in the water? Is part of the rationale specific to flamingos? If so, why? Are there other reasons?

Lake Nakuru is referred to in this paper as a highly alkaline lake. Although the lake is basic, with a pH of 10, water alkalinity is not directly related to the water pH, but instead to its buffering capacity. Alkalinity is determined by assessing the ability of the water to neutralize added acid. It is typically calculated as the total alkalinity (A_T). Because carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) are usually the most significant components in natural waters, alkalinity is measured by titrating a water sample with a strong acid until pH 4.5 where bicarbonate or carbonate has been consumed. Although the most important determinant of alkalinity is the amount of carbonate, other weak bases can also contribute to total alkalinity, as indicated below. Because of its importance in many surface waters, A_T is normally expressed as mg/L CaCO_3 , even though this unit is not particularly meaningful for Lake Nakuru, as Nelson et al. report a $[\text{Ca}^{2+}]$ of 0 in Table 1.

$$A_T = [\text{HCO}_3^-] + 2 \times [\text{CO}_3^{2-}] + [\text{SO}_4^{2-}] + 2 \times [\text{PO}_4^{3-}] + [\text{F}^-] + [\text{NH}_3] + [\text{OH}^-] - [\text{H}^+]$$

You will notice that in the equation for A_T some ions are multiplied by a factor of two, and that this factor is not related to their charge. Alkalinity can be measured by titrating a sample with a strong acid until the buffering capacity of the ions is consumed. Normally, environmental water samples are buffered by CO_3^{2-} and HCO_3^- so the endpoint of the alkalinity titration is functionally set to pH 4.5. The $[\text{CO}_3^{2-}]$ is multiplied by 2 as two moles of H^+ would be required to fully neutralize the carbonate ion. The $[\text{SO}_4^{2-}]$ is multiplied by a factor of 1 because it would not be converted to H_2SO_4 under the conditions of the titration. Similarly $[\text{PO}_4^{3-}]$ would not be converted only to H_2PO_4^- at pH 4.5 therefore it is multiplied only by a factor of 2.

Q3. Why do you think that $[\text{F}^-]$ is included in this calculation, while $[\text{Cl}^-]$ is not?

Q4. Using the data in Table 1 (Nelson, 1998), calculate the alkalinity of the Lake Nakuru, in mg/L CaCO₃.

The Methods section of the Nelson paper suggests that the water samples collected may not have been acidified, although, acidification with 5% nitric acid is often used to stabilize water samples especially those collected for metal ion analysis ([EPA-1669, 1996](#)). If samples are to be measured separately for dissolved metals they should be filtered before acidification.

Q5. Why could it be important to filter suspended particles or sediment from the water sample before acidification?

Section 8.4.3 of EPA method 1669 says “Preservation of aliquots for metals other than trivalent and hexavalent chromium—Using a disposable, precleaned, plastic pipet, add 5 mL of a 10% solution of ultrapure nitric acid in reagent water per liter of sample. This will be sufficient to preserve a neutral sample to pH <2.”

Q6. Assume that you collect and filter a 1 liter water sample from Lake Nakuru. Using the total alkalinity you calculated in **Q4**, would addition of 5 mL of 10% nitric acid reduce the pH of your water sample to < 2? If not, how do you suggest that this protocol should be altered?

The paper by Nelson et al. examines adsorption to both particulate matter and the algae. The particulate matter was derived from sediment samples collected from Lake Nakuru at the locations where the water samples were collected. The algae *Spirulina platensis* was grown in the laboratory under conditions similar to those in Lake Nakuru. For the results for binding to the suspended sediments, the authors write:

“Adsorption isotherms for metal adsorption to Lake Nakuru sediments in reconstituted lake water at pH 10.0 were linear for all four metals with respect to dissolved metal concentration over the range of concentrations considered, and distribution coefficients (K_d) were calculated for each metal (Fig. 1).”

Q7. Examine the results presented in Figure 1 of the paper by Nelson et al. Why do you think that the experimental results deviate most from the line at low concentrations of the dissolved metal?

Q8. For adsorption to algae (Figure 2 of Nelson et al.) the adsorption behavior is not linear. The authors suggest that the results for Cr, Cu and Zn are consistent with that of a Langmuir isotherm ([click here](#) for a tutorial on the Langmuir isotherm).

SUMMARY

The paper by Nelson et al. provides an excellent entry point for our consideration of the possible effect of toxic metals on the flamingos at Lake Nakuru. It should now be clear to you that flamingos are exposed to metals primarily by filtering suspended sediments along with their food supply. The next unit will allow you to develop a plan for the analysis of heavy metals that are adsorbed on the suspended sediment found in Lake Nakuru. Several analytical approaches will

be considered: x-ray fluorescence analysis (XRF), atomic spectroscopy (FLAAS, GFAA, and ICP-AES), and anodic stripping voltammetry (ASV).

REFERENCES

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Y. M. Nelson, R. J. Thampy, G. I. K. Motelin, J. A. Rani, C. J. Disante, L. W. Lion *Environ. Toxicol. Chem.* **17**:2302–230 (1998).

EPA Method 1669 “Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels” (1996) http://www.hydroqual.com/pdf/B_1669%20clean%20sampling.pdf, accessed June 22, 2011.