

Review of: Mongelli, G., Monni, S., Oggiano, G., Paternoster, M., and Sinisi, R., 2013, Tracing groundwater salinization processes in coastal aquifers: a hydrogeochemical and isotopic approach in Na-Cl brackish waters of north-western Sardinia, Italy: *Hydrology and Earth System Sciences Discussions*, v. 10, p. 1041-1070.

By

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The data set in this paper for the Na-Cl brackish waters of north-western Sardinia, Italy, is valuable with data for all samples for oxygen-18 and deuterium isotopes in water, and sulfur-34 and oxygen-18 isotopes in sulfate as well as data for water chemistry. The purpose of this expanded data set is to identify whether the brackish ground water is created by mixing of rain water with sea water and/or from water-rock interaction. Unfortunately, the mixing line between sea water and rain water for oxygen-18 in water and chloride was calculated incorrectly in their Fig. 6, and this changes the interpretation for the source of chloride. In addition, a comment is added on the possibility of oxygen-18 in sulfate being changed by incomplete equilibrium between sulfate and water.

The mixing line for sea water and rain water in Figure 6 is incorrect, and it is unclear exactly how it was calculated. The correct formula is:

$$(\delta^{18}\text{O})_m = x (\delta^{18}\text{O})_{\text{sw}} + (1 - x) (\delta^{18}\text{O})_{\text{rw}} \quad (1)$$

where  $x$  is the fraction of sea water, and the subscripts are m for mixture, sw for sea water, and rw for rain water. A similar formula holds for dissolved constituents such as chloride and sulfate. Fig. N-1 shows the well and spring waters along with mixing lines. The solid line uses the rain-water isotope value reported in this paper from a single sample. The line does not extend through the data. It is standard procedure to estimate the rain-water end member for such a mixing line from spring and well samples rather than from a single rain-water collection. The spring and well samples can be derived from mixing sea water with rain water that has  $\delta^{18}\text{O}$  in the range of  $-6.6 \pm 0.5$  ‰ as shown in Fig. N-1. The reported laboratory uncertainty for oxygen-18 is  $\pm 0.2$  ‰, and the uncertainty for the rain-water end member is larger indicating that there may be some variability in the rain-water end member around the area. The behavior in Fig. N-1 disagrees with the conclusion in the paper based on the incorrect mixing line in their Fig. 6 that oxygen-18 isotopes and chloride cannot be explained by mixing.

The question then becomes the source of sulfate in the well and spring waters given that we can explain chloride and water isotopes by mixing of rain water and sea water. Fig. N-2 shows sulfate versus chloride (similar to their Figure 4). Many of the sulfate values do not match the model of sulfate coming from mixing of rain water and sea water. Some have higher sulfate whereas a couple have lower sulfate indicating that there could be dissolution or precipitation of gypsum.

For isotopes in sulfate dissolved in water, the mixing equation is different:

$$(\delta^{34}\text{S-SO}_4)_m = [x (\text{SO}_4)_{sw} (\delta^{34}\text{S-SO}_4)_{sw} + (1 - x) (\text{SO}_4)_{rw} (\delta^{34}\text{S-SO}_4)_{rw}] / (\text{SO}_4)_m \quad (2)$$

where  $(\text{SO}_4)$  is the dissolved sulfate,  $(\delta^{34}\text{S-SO}_4)$  is the sulfate isotopic value, and the subscripts are the same as for eq. (1). Fig. N-3 shows  $\delta^{34}\text{S-SO}_4$  for the wells and springs along with the mixing line. The mixing line is a pretty good match to some but not all of the data. The deviation from the mixing model could be explained by exchange with or addition of  $\text{SO}_4$  from gypsum in the subsurface, since the values for solids reported in the table are around 15 ‰.

The paper presents a model that the sulfate could be derived from dissolving sulfate from various rock sources. The equation for adding isotopes in sulfate minerals to rain water is:

$$(\delta^{34}\text{S-SO}_4)_m = [(\text{SO}_4)_{rw} / (\text{SO}_4)_m] (\delta^{34}\text{S-SO}_4)_{rw} + [1 - (\text{SO}_4)_{rw} / (\text{SO}_4)_m] (\delta^{34}\text{S-SO}_4)_a \quad (3)$$

where  $(\delta^{34}\text{S-SO}_4)_a$  is for the isotopic value of the added sulfate. This model is shown in Fig. N-4. This model also explains the data. It is likely that both models are involved in setting the sulfur-34 isotopes, because both mixing and rock-water interaction appear to be taking place for sulfate.

The oxygen-18 isotopes in sulfate are a problem. Fig. N-5 shows  $\delta^{18}\text{O-SO}_4$  along with the mixing line. A few data points agree with the mixing line, but most do not. The  $\delta^{18}\text{O-SO}_4$  in the solid samples in the authors' Table 2 range from 10.4 to 11.6 ‰, and their values cannot explain the much more positive values found for  $\delta^{18}\text{O-SO}_4$ . Groundwater residence times, especially for samples obtained from wells, could be many 10s to 100s of years. One possibility is that the  $\text{SO}_4$  in water is trying to equilibrate its  $^{18}\text{O}$  isotopes with that in water, and this reaction would result in the  $\delta^{18}\text{O-SO}_4$  values becoming more positive until equilibrium is attained. The reaction time at 20°C and pH 7 to achieve one half of equilibrium is 3,600 years (McKenzie and Truesdell, 1977), though the data in Chiba and Sakai (1985) indicate that reaction times could be much longer at low temperatures. Using the second equation at the end of McKenzie and Truesdell (1977) for an average  $\delta^{18}\text{O}$  in water for the samples of -6.1 ‰, the  $\delta^{18}\text{O-SO}_4$  would be 24.3 ‰, though it should be recognized that the equation for isotopic equilibrium was not calibrated for such a low temperature. The  $\delta^{18}\text{O-SO}_4$  value of 24.3 ‰ for isotopic equilibrium is consistent with the values for some waters having achieved partial isotopic equilibrium indicating that some water samples are pretty old.

#### References cited

McKenzie, W.F., and Truesdell, A.H., 1977, Geothermal reservoir temperatures estimated from the oxygen isotope compositions of dissolved sulfate and water from hot springs and shallow drillholes: *Geothermics*, v. 5, p. 51-61.

Chiba, H., and Sakai, H., 1985, Oxygen isotope exchange rate between dissolved sulfate and water at hydrothermal temperatures: *Geochimica et Cosmochimica Acta*, v. 49, p. 993–1000.

Figure captions

Figure N-1. Plot of oxygen-18 isotopes in water versus chloride concentration in water.

Mixing lines between rain water and sea water for two values of oxygen-18 isotopes in rain water with data for springs and wells. Mixing line is non-linear because of log scale for chloride.

Figure N-2. Plot of sulfate versus chloride concentration in water for springs and wells along with mixing line between rain water and sea water. Sea-water values are beyond the range of the plot.

Figure N-3. Plot of sulfur-34 isotopes in sulfate in water versus sulfate concentration in water for springs and wells along with mixing line between rain water and sea water.

Figure N-4. Plot of sulfur-34 isotopes in sulfate in water versus sulfate concentration in water for springs and wells along with lines for adding sulfate to water with several isotopic contents. Values for isotopes of Triassic evaporites given in the caption to the authors' Fig. 9.

Figure N-5. Plot of oxygen-18 isotopes in sulfate in water versus sulfate concentration in water for springs and wells along with mixing line between rain water and sea water.

# Mix rain water and sea water

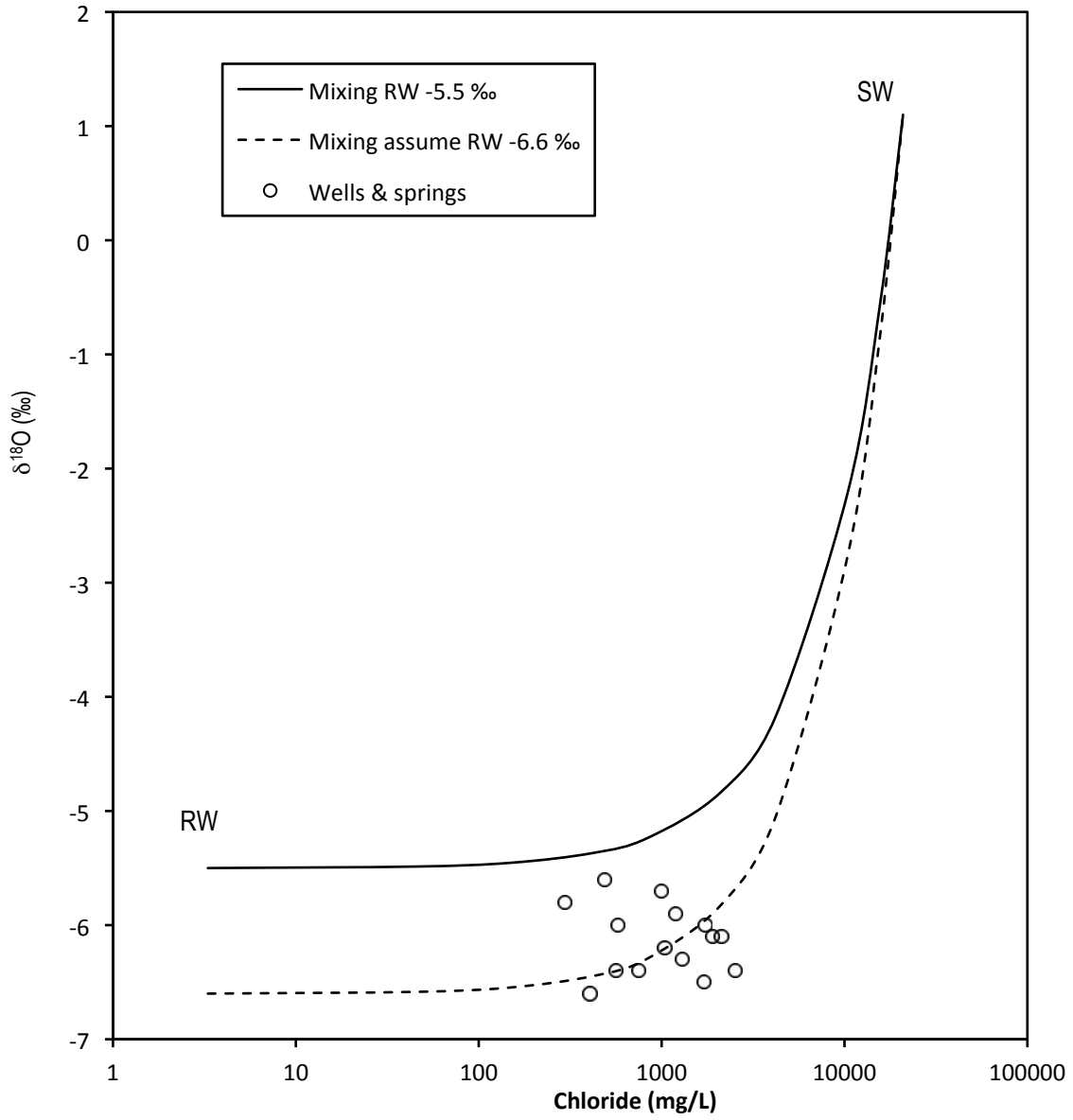


Figure N-1

# Mix rain water and sea water

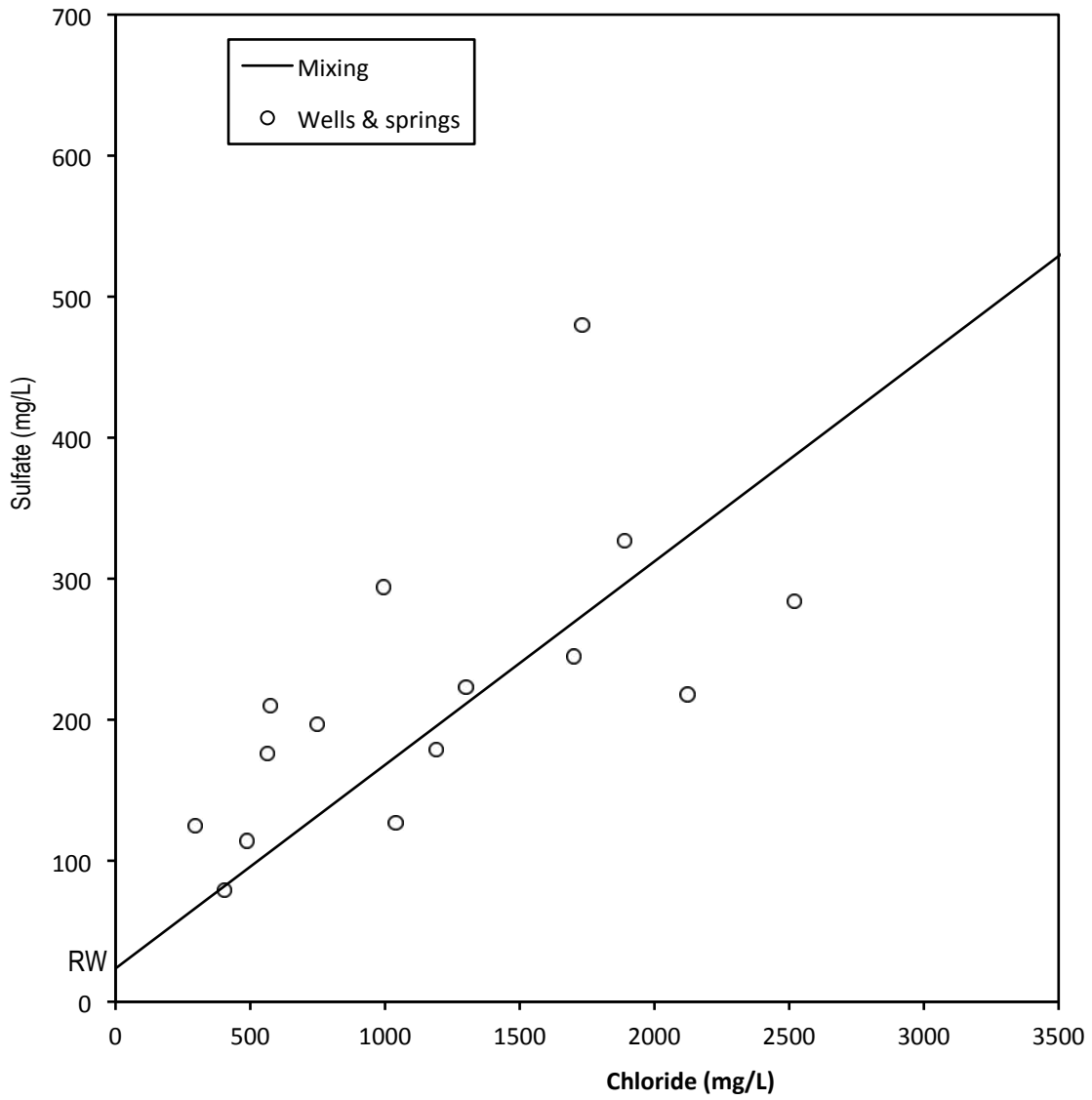


Figure N-2

# Mix rain water and sea water

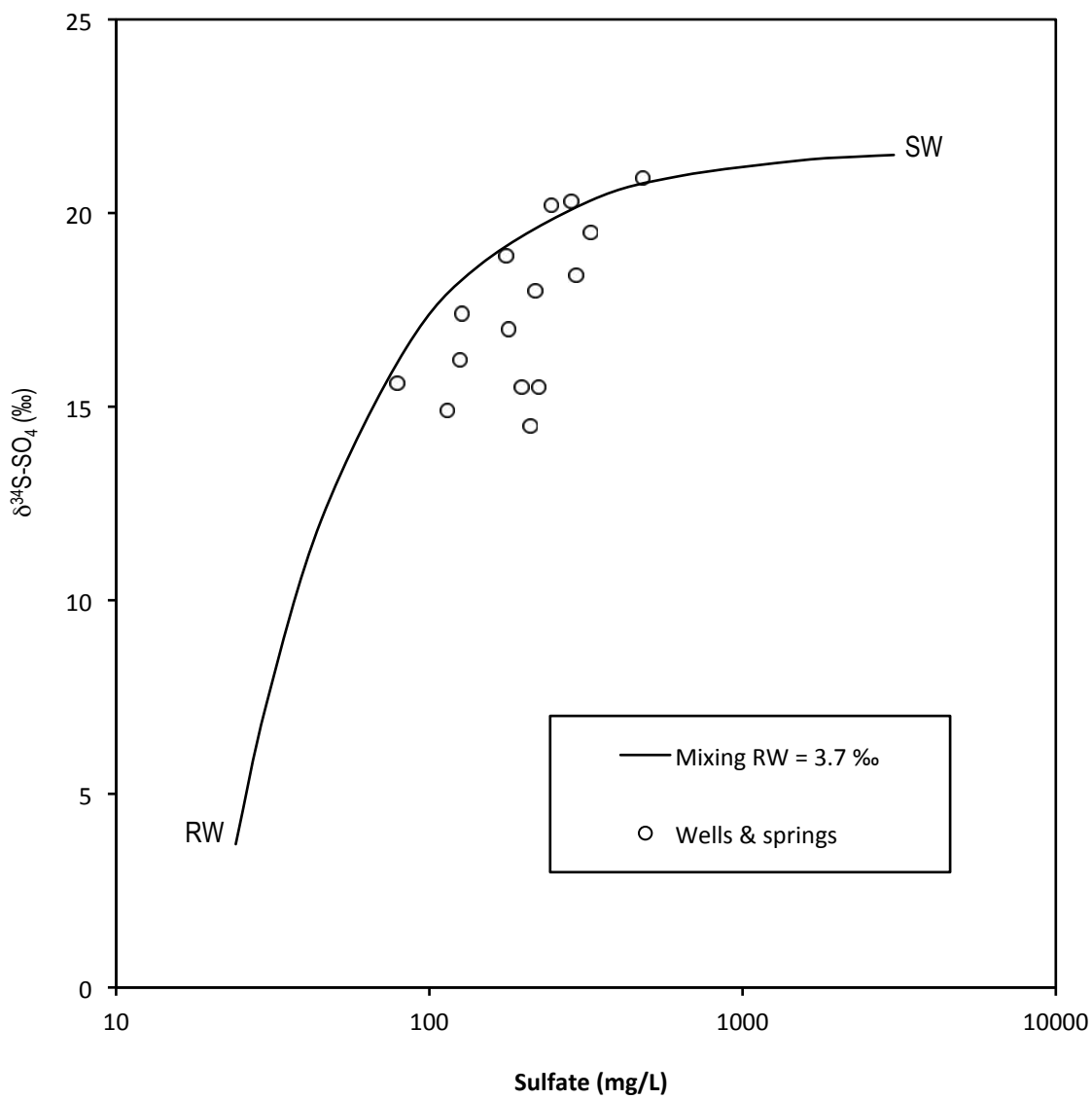


Figure N-3

# Add sulfate to rain water

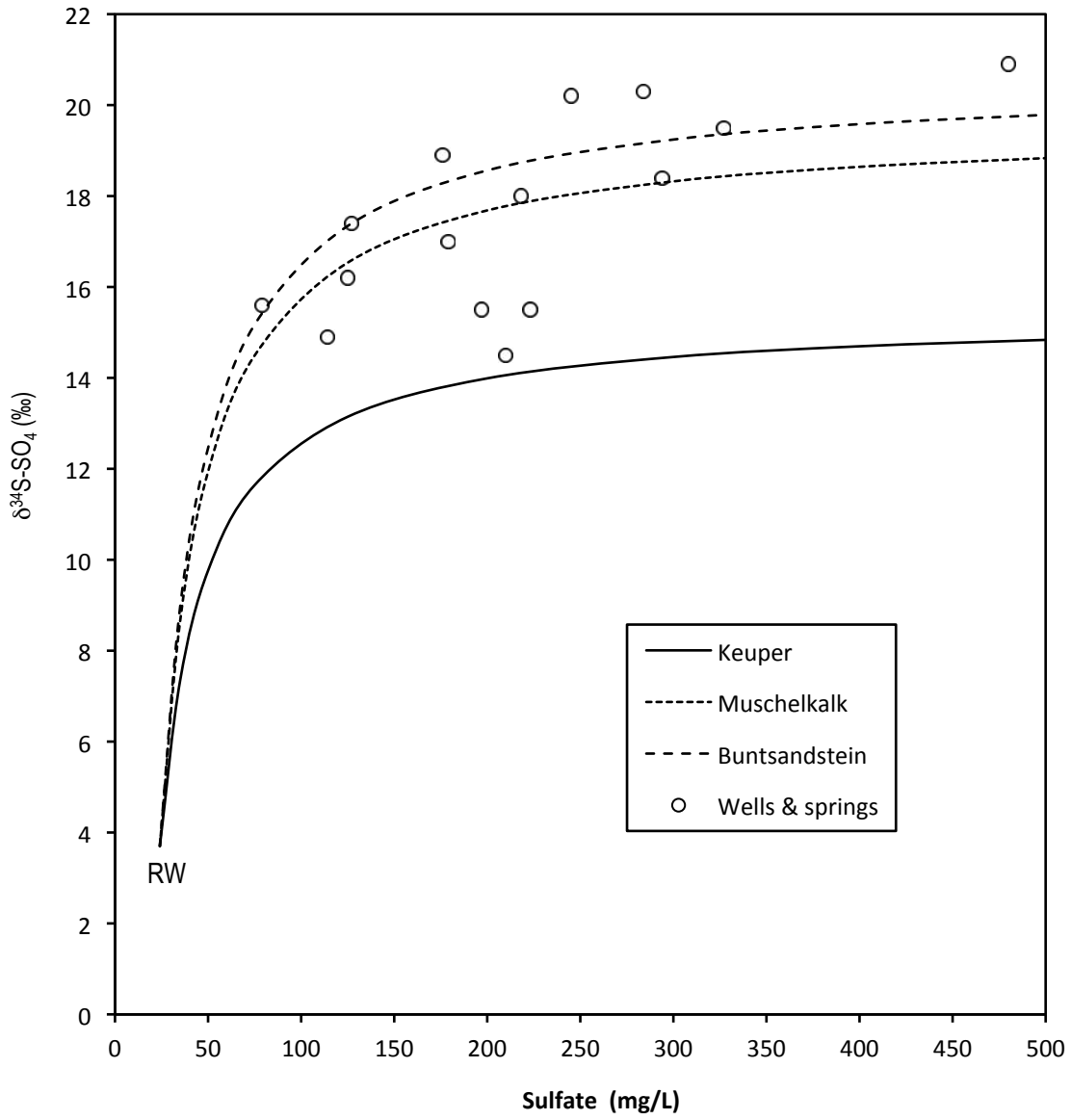


Figure N-4

# Mix rain water and sea water

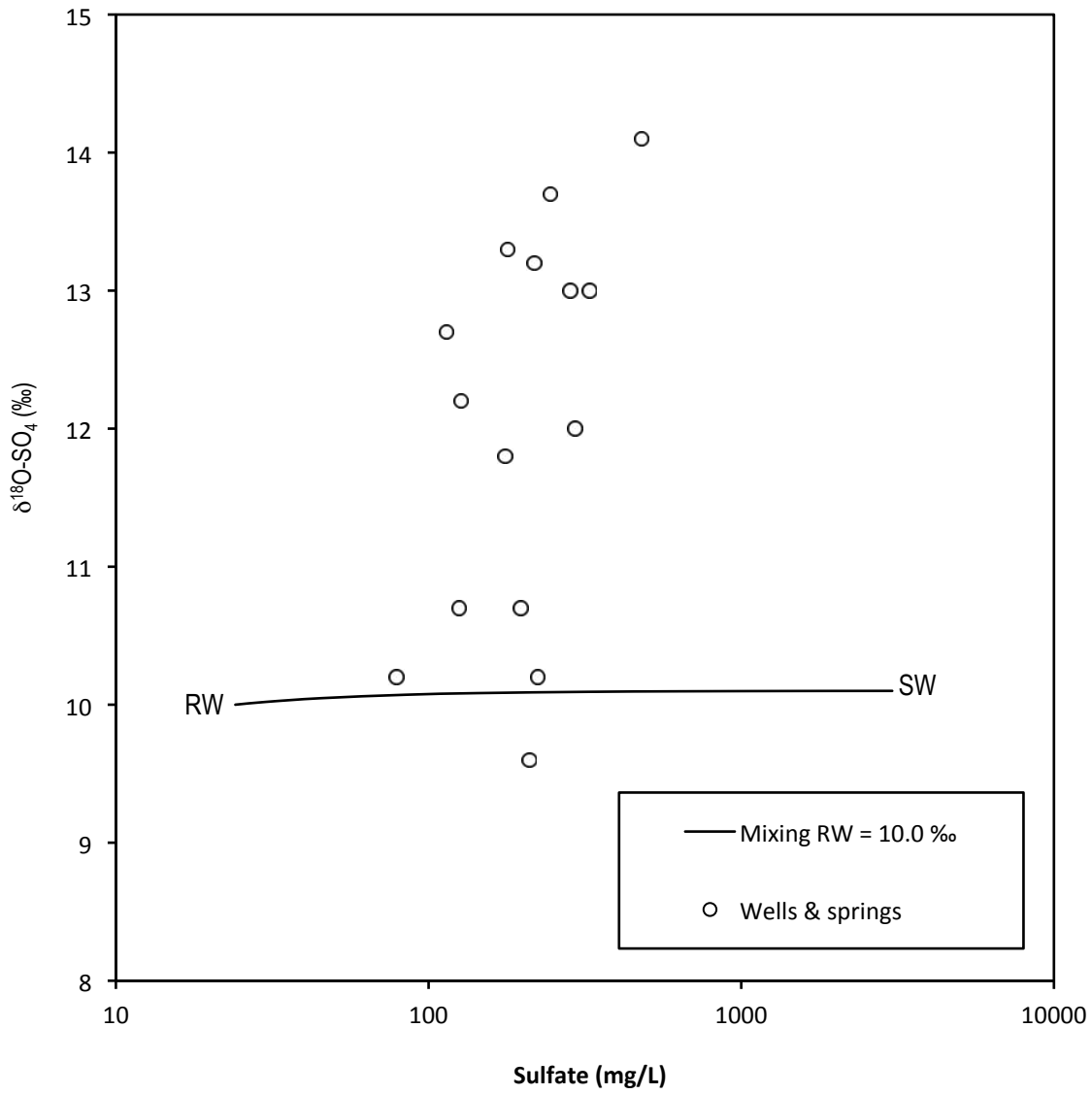


Figure N-5