



Identifying karst water sulfate and nitrate sources by combined use of isotopic and ionic ratios

Ya Wu, Yanxin Wang, and Teng Ma

China University of Geosciences, School of Environmental Studies, Environmental science and engineering, Wuhan, China
(wuya@cug.edu.cn)

Combined use of $\delta^{34}\text{S}$ and $\text{Ca}^{2+}/\text{Na}^{+}$ molar ratio and $\delta^{15}\text{N}$ and $\text{NO}_3^-/\text{Na}^{+}$ ratio may identify karst water SO_4^{2-} and NO_3^- sources. With characteristic isotopic and ionic ratios from China, especially Guizhou province, the relevant end-members are determined as follows. Rainwater may have $\delta^{34}\text{S}$, $\delta^{15}\text{N}$, $\text{Ca}^{2+}/\text{Na}^{+}$, and $\text{NO}_3^-/\text{Na}^{+}$ values/ratios of -4.0 to -0.8‰ (average -5.4‰ , -0.81‰ , 22.5, and 10.7, respectively (Hong et al., 1993; Wu et al., 2018). They could be -2.01 to -2.51‰ (average -7.52‰ for $\delta^{34}\text{S}$ and 0.0 – 1.5 (average 0.4 ± 0.5) for $\text{Ca}^{2+}/\text{Na}^{+}$ in terms of waters leaching coal (Hong et al., 1993; Li et al., 2018). Waters draining carbonates and gypsum are probably characterized by $\delta^{34}\text{S}$ values of 14.5 – 32.5‰ with $\text{Ca}^{2+}/\text{Na}^{+}$ ratios of 50 – 200 and 13.2 , respectively (Chen and Chu, 1988; Gaillardet et al., 1999; Huang et al., 2016). For waters affected by chemical fertilizers, $\delta^{34}\text{S}$ values of -5.6 to 7.7‰ (average -0.8‰ and a $\text{Ca}^{2+}/\text{Na}^{+}$ ratio of 279 are likely related to superphosphate; $\delta^{15}\text{N}$ values of -5.61 to 3.98‰ (average $-0.35 \pm 1.90\text{‰}$ and 1.91 to 21.33‰ (average $8.69 \pm 5.78\text{‰}$ represent NH_4^{+} in chemical fertilizer and NO_3^- in NH_4NO_3 fertilizer, respectively, with $\text{NO}_3^-/\text{Na}^{+}$ ratios of ~ 10 (Cao et al., 1991; Li et al., 2006; Roy et al., 1999; Rui et al., 2008). Waters leaching red soil may show $\delta^{15}\text{N}$ values and $\text{NO}_3^-/\text{Na}^{+}$ ratios of 1.00 to 1.56‰ (average $1.29 \pm 0.20\text{‰}$ and 2.4 – 5.3 , respectively (Cao et al., 1993; Wu et al., 2018). The $\delta^{15}\text{N}$ values of 7.47 to 49.71‰ caused by human waste, with $\text{NO}_3^-/\text{Na}^{+}$ ratios of 0.01 to 0.38 may be assigned to domestic sewage (Wu et al., 2018; Xing et al., 2001).

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