

Stream water chemistry and dynamics of sulfur derived from atmospheric deposition in a forested catchment in central Japan

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[Introduction]

Ijira catchment is located in the downwind side of the Chukyo Industrial Area in central Japan and has been historically experiencing large-scale depositions of sulfur and nitrogen from the atmosphere. The catchment was acidified and nitrogen-saturated in the mid-1990s, according to previous studies (Yamada et al. 2007; Nakahara et al. 2010). However, recovery from acidification and nitrogen saturation has been observed recently.

[Methods]

We used the following monitoring data from the Ministry of the Environment of Japan: long-term data of stream water chemistry since 1988, wet deposition (rainwater) monitoring data since 2000, the input-output budget since 2007, and isotopic data of sulfur and strontium in rainwater, soil solution and stream water since 2014. Moreover, sulfur isotopic data of tree rings in *Cryptomeria Japonica* from the Chukyo Area was also used for analysis of long-term trends on stream water chemistry and dynamics of sulfur derived from atmospheric deposition in the forested catchment.

[Results and discussion]

The stream water pH declined from 7.3 in 1994/1995 to 6.6 in 2003, and then promptly recovered to a value of approximately 7 thereafter. Simultaneously, the NO_3^- concentration increased until 2002/2003 and thereafter started declining in 2005. During the period of acidification with NO_3^- leaching, the SO_4^{2-} concentration reached the highest value in 1994 with a mean concentration of $210 \mu\text{mol}_c \text{L}^{-1}$, and then gradually declined to $127 \mu\text{mol}_c \text{L}^{-1}$ in 2013. In addition, the concentrations of dissolved organic carbon were high from the mid-1990s to the early-2000s. The mean annual SO_4^{2-} input from 2007 to 2012 was $0.9 \pm 0.1 \text{ kmol}_c \text{ ha}^{-1} \text{ year}^{-1}$, while the mean annual output from the stream for the corresponding period was $2.3 \pm 0.5 \text{ kmol}_c \text{ ha}^{-1} \text{ year}^{-1}$. Even after taking into account various uncertainties, the output of SO_4^{2-} exceeded the input. The mean sulfur isotopic ratios ($\delta^{34}\text{S}$) of SO_4^{2-} in rainwater and soil solution at 20 cm depth were 4.6‰ and 3.8‰, respectively, while that in the stream water was -13‰. Recent sulfur inputs appear to be retained in relatively shallow soil layers. The sulfur in shallow layers may have contributed to the high concentrations in the mid-1990s. Reports in the literature suggest the existence of geological sources with significantly low $\delta^{34}\text{S}$ values (from -14‰ to -8‰) near the study catchment. Therefore, it is possible that the SO_4^{2-} derived from geological sources contributes to the large discrepancy, although dendrochronology suggests certain effects of the atmospheric inputs with lower $\delta^{34}\text{S}$ (from -7‰ to +1‰) in the 1960s/1970s in the Chukyo Industrial Area.

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[References]

Nakahara et al. 2010. *Biogeochemistry* 97: 141-158.

Yamada et al. 2007. *Water, Air, and Soil Pollution: Focus* 7: 259-266.

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