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 $\mu mol_c\ L^{-1}$, and then gradually declined to 127 $\mu mol_c\ L^{-1}$ 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 ±0.1 $kmol_c\ ha^{-1}\ year^{-1}$, while the mean annual output from the stream for the corresponding period was 2.3 ±0.5 $kmol_c\ ha^{-1}\ year^{-1}$. Even after taking into account various uncertainties, the output of SO_4^{2-} exceeded the input. The mean sulfur isotopic ratios ($\delta^{34}S$) 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 $\delta^{34}S$ 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 $\delta^{34}S$ (from −7‰ to +1‰) in the 1960s/1970s in the Chukyo Industrial Area.
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