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SPECIAL FEATURE: ORIGINAL ARTICLE

Phosphorus cycle in watersheds

Factors characterizing phosphate oxygen isotope ratios in river water: an inter-watershed comparison approach

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Abstract

We compared the oxygen isotope ratio of dissolved phosphate $\left(\delta^{18}O_{PO_4}\right)$ in two rivers with different land-cover and geological features (Ado River and Yasu River) within Lake Biwa basin, central Japan, to explore what factor primarily characterizes the $\delta^{18}O_{PO_4}$. Mean values of $\delta^{18}O_{PO_4}$ in river water were 19.0 ± 2.4‰ ($n = 7$) in Ado River and 13.1 ± 2.3‰ ($n = 15$) in Yasu River, which were significantly different. Comparisons of $\delta^{18}O_{PO_4}$ between river water and potential sources of phosphate revealed that in the Ado River, the $\delta^{18}O_{PO_4}$ was similar to that in rocks from the accretionary complex and decreased with increasing sedimentary rock coverage. In the Yasu River, the $\delta^{18}O_{PO_4}$ was low in the upper forested areas, but increased with paddy field coverage. These results demonstrate that river $\delta^{18}O_{PO_4}$ strongly reflects inputs from geological substances, but is also impacted by land-use activities and varies with anthropogenic land coverage in the watershed. Thus, river $\delta^{18}O_{PO_4}$ relates to land or bedrock coverage differentially in each river. Regression analysis showed that residuals of the $\delta^{18}O_{PO_4}$ tended to converge to zero with increasing drainage area, suggesting that river $\delta^{18}O_{PO_4}$ more explicitly reflects land-cover and geological features on a larger watershed scale.

Keywords Hydrological processes · Non-point source pollution · Oxygen isotopes in phosphate · Isotope tracers

Introduction

Phosphorus (P) is an essential element for all living organisms and an important resource for food production. On the other hand, the supply of mineral P is finite and is decreasing while world consumption of P resources is gradually increasing (USGS 2016). Anthropogenic utilization of P resources has resulted in excess P loadings from land to water bodies (Steffen et al. 2015). This may induce eutrophication in receiving waters, i.e., lakes, reservoirs, estuaries, and the coastal sea, which can cause damaging environmental issues, such as, algal blooms, red tides, and the elimination of fish habitat (Duce et al. 2008). Diaz and Rosenberg (2008) reported that more than 400 coastal dead zones exist throughout the world and many of them were found at the

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mouths of rivers discharging high P loads. To prevent excess P loading and facilitate the efficient utilization of P resources in terrestrial ecosystems, we need to better understand P dynamics and specifically identify sources of P for waterways, linking them to land use and land cover management as well as to the geology on a watershed scale.

Many studies have evaluated P loading to receiving waters by measuring the total P concentration in river water and river flow volume from individual watersheds (Dolan et al. 1981; House et al. 1997; Ide et al. 2012; Kronvang and Bruhn 1996; Vanni et al. 2001). These estimations are important when detecting trends in annual transport rate of P, estimating the mass balance of P in receiving waters, and exploring best management practices to reduce excess P loading from the point and nonpoint sources (Alvarez-Cobelas et al. 2009). However, they do not allow us to identify the sources of P to waterways within a watershed. While several studies have evaluated relationships between P concentrations and land cover and land use (Brett et al. 2005; Ide et al. 2019; Jordan et al. 1997; Salvia-Castellví et al. 2005), they also do not provide us decisive information on what the dominant source contributing to increased P loading is.

Recently, an analysis based on the oxygen isotope ratio of phosphate $\left(\delta^{18}O_{PO_4}\right)$ has been suggested as a tool to explore P dynamics in diverse water bodies (Colman et al. 2005; Elsbury et al. 2009; Markel et al. 1994; McLaughlin et al. 2006a, b, c). The phosphorus–oxygen (P–O) bond in phosphate (PO_4^{3-}) is resistant to inorganic hydrolysis at earth's typical surface temperature and pressure and does not exchange oxygen with ambient water without biological enzymatic mediation that cleaves the P–O bond and thereby causes large isotopic fractionation (Blake et al. 1997; Chang and Blake 2015; Lécuyer et al. 1996; Longinelli and Nuti 1973; Paytan and McLaughlin 2012). This indicates that the $\delta^{18}O_{PO_4}$ in river water is expected to reflect the isotopically distinct sources of PO_4^{3-} where P utilization rates by organisms are small compared to the P input (Young et al. 2009). It is, therefore, possible to link P dynamics in river water to land cover and/or geology within a watershed using the $\delta^{18}O_{PO_4}$. Indeed, a few studies have reported $\delta^{18}O_{PO_4}$ in rivers and have shown that the $\delta^{18}O_{PO_4}$ was different between rivers with different geographical features (Granger et al. 2017; McLaughlin et al. 2006a; Tonderski et al. 2017; Young et al. 2009). Young et al. (2009) investigated the range of the $\delta^{18}O_{PO_4}$ values in the Lake Erie tributaries, the San Joaquin River and tributaries, and the Lake Tahoe tributaries and showed that the mean $\delta^{18}O_{PO_4}$ value was significantly lower in the Lake Tahoe tributaries than in the other river and tributaries. It is also expected that the $\delta^{18}O_{PO_4}$ in river water will reflect the $\delta^{18}O_{PO_4}$ of the dominant bedrock types in a pristine watershed, because some of the PO_4^{3-} in river water derives from rock weathering (Walker and Syers 1976). However, few studies have applied the $\delta^{18}O_{PO_4}$ technique to river watersheds in Japan, which are characterized by large forest coverage within mountainous terrain. This is because a large sample size and time-consuming and laborious work would be required for such $\delta^{18}O_{PO_4}$ analysis due to low concentrations of dissolved PO_4^{3-} in river water (McLaughlin et al. 2004; Paytan and McLaughlin 2012). Ishida et al. (2019) first investigated the spatial pattern of $\delta^{18}O_{PO_4}$ in river water on a watershed scale in Yasu River, Japan, and revealed that the variability in $\delta^{18}O_{PO_4}$ could be generally explained by land and bedrock coverage in the watershed. However, they applied the $\delta^{18}O_{PO_4}$ technique to just one watershed with complex land-cover and geological features. Thus, it remains unclear whether the relationship between river $\delta^{18}O_{PO_4}$ and watershed land cover and geology can be generalized. Particularly, little information is available regarding the $\delta^{18}O_{PO_4}$ in pristine watersheds with simple land-cover and geological features and what factors primarily controls this value.

Because P is transported mainly as dissolved and particulate loads by water but not converted into gas phase (Elser and Benett 2011), it moves from land to surface waters in a one-way direction. Therefore, the $\delta^{18}O_{PO_4}$ in river water is predicted to be strongly affected by water flowpath. Several studies have shown that losses of P from a watershed occur along hydrological surface and subsurface pathways (e.g., Ide et al. 2008; McDonnell et al. 2010; Sharpley et al. 2015). Tonderski et al. (2017) investigated the $\delta^{18}O_{PO_4}$ in river water from an agricultural watershed located in southeast Sweden at different hydrological regimes and indicated that fertilization practices, hydrological conditions, and water flowpath have a critical influence on the spatial variations in $\delta^{18}O_{PO_4}$ signatures. They emphasize the importance of water flowpath because the transport of P from different soil layers could result in variations in $\delta^{18}O_{PO_4}$ signatures. Uchida and Asano (2010) showed that streamflow was a mixture of water originating from soil water and from bedrock groundwater in a meso-scale watershed and that the depth of runoff sources and the relative contribution of water emerging from bedrock groundwater varied spatially depending on watershed area. This indicates that the depth of flowpath is a key component describing watershed hydrological and geochemical responses. Since the $\delta^{18}O_{PO_4}$ in river water would strongly reflect isotopically distinct sources of PO_4^{3-}, such as fertilizer and bedrock, it is expected that the $\delta^{18}O_{PO_4}$ will be affected by the flowpath, resulting in signatures that could not be explained by the land-cover and geological features alone.

Many studies have used dissolved silica (SiO_2) concentrations to examine the water flowpath and estimate the origin of water drained from a watershed (Buttle and Peters 1997; Hinton et al. 1994; Hooper and Shoemaker 1986; O'Brien and Hendershot 1993; Scanlon et al. 2001; Wels et al. 1991). SiO_2 is one of the conservative solutes not measurably

affected by biological reactions, and sources of SiO_2 are almost exclusively soil and bedrock minerals. The SiO_2 concentration draining from a watershed thus can reflect the depth of the water sources, i.e., flowpath contributing to the main river water (Asano et al. 2003; Uchida et al. 2008). Therefore, SiO_2 can be used as a tracer of hydrological flowpath to clarify the cause of variations in the $\delta^{18}O_{PO_4}$ signatures on a watershed scale.

In this study, we aimed to examine what factors primarily characterize the $\delta^{18}O_{PO_4}$ in the watersheds with mountainous terrain with a focus on the following hypotheses:

1. The river $\delta^{18}O_{PO_4}$ reflects the dominant bedrock $\delta^{18}O_{PO_4}$ in a pristine watershed.
2. The relationship between the river $\delta^{18}O_{PO_4}$ and factors explaining its variability, i.e., land cover and geological setting are consistent, independent of individual watersheds.
3. Water flowpath partially explains observed variability of the river $\delta^{18}O_{PO_4}$.

For this, we collected water samples from two rivers with different land-cover and geological features, located in central Japan, and compared the $\delta^{18}O_{PO_4}$ between the rivers. We also collected samples of potential sources of PO_4^{3-}, such as fertilizer, sewage treatment water, and rocks, and compared the $\delta^{18}O_{PO_4}$ between river water and potential sources. Additionally, we measured the SiO_2 concentration in river water.

Materials and methods

Site descriptions

This study was conducted in two rivers, Ado River and Yasu River, which belong to the Lake Biwa–Yodo River system, located in Shiga Prefecture (Ado River: 34° 15′ N–35° 41′ N, 135° 76′ E–136° 07′ E, Yasu River: 34° 50′ N–35° 10′ N, 136° 0′ E–136° 30′ E; Fig. 1), central Japan. The climate of the two river watersheds is humid temperate. Annual precipitation varies from approximately 1700 to 2000 mm in

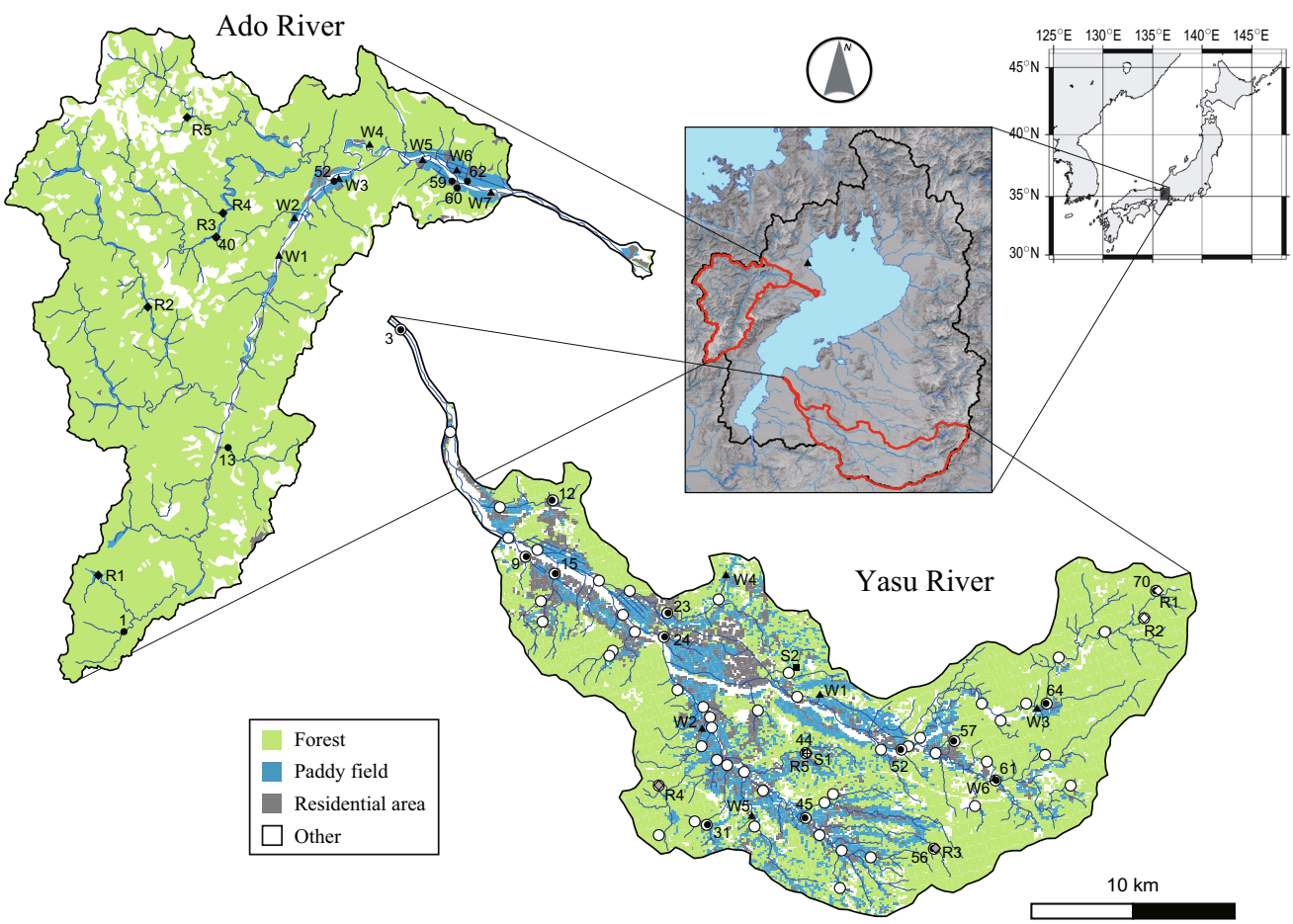

Fig. 1 The location and map of study sites showing sampling sites and land cover. Closed circles, diamonds, triangles, and squares in the figure represent sampling points of river water, rocks, sewage treatment water, and paddy field soils, respectively. Open circles represent sampling points of river water for the silica concentration analysis

the Ado River watershed, and from approximately 1500 to 1800 mm in the Yasu River watershed (Ohte et al. 2010).

Ado River is the second largest river flowing into Lake Biwa, with a watershed area of 311 km^2, and the length of the main river channel is approximately 56 km. The altitude ranges from 85 to 1214 m above sea level. The Ado River watershed is mostly occupied by forests (92%), whereas agricultural and residential areas account for 4% and 1% of the land use in the watershed, respectively. The underlying bedrock is mostly accretionary complex rock. The accretionary complex rock contains igneous and biogenic apatite as it is composed of marine sediments accreted onto a non-subducting tectonic plate at a convergent boundary (Isozaki et al. 1990).

Yasu River is the largest river flowing into Lake Biwa, with a watershed area of 387 km^2, and the length of the main river channel is approximately 65 km. The altitude ranges from 86 to 1212 m above sea level. Upstream areas of the watershed are mainly composed of forests, whereas downstream areas are composed of the residential area surrounded by agricultural lands. Forest, agricultural, and residential areas account for approximately 55%, 24%, and 11% of the watershed area, respectively. The dominant agriculture use in the watershed is rice paddy. The underlying bedrock is either sedimentary rock or granite, which is distributed along the main river channel and around the southern and eastern parts of the watershed, respectively. Additionally, the accretionary complex rock is distributed upstream. The sedimentary rocks could contain biogenic apatite, oxides and organic matter, which are common in marine sediments (Crook et al. 2018).

Sample collection and preparation

We collected 7 and 15 water samples in the tributaries and main channels of Ado River and Yasu River, respectively, for analysis of the $\delta^{18}O_{PO_4}$ (Fig. 1). We also collected 67 water samples for analysis of SiO_2 in Yasu River. The water sampling was conducted in September 2014 and September 2015 in Ado River, and in May 2016 in Yasu River. Sample volume for the analysis of the $\delta^{18}O_{PO_4}$ ranged from 20 to 180 L, depending on soluble reactive phosphorus (SRP) concentrations, which were measured prior to the sampling campaign in the laboratory. Because more than 100-L water samples were required in some tributaries of Ado River for the analysis of the $\delta^{18}O_{PO_4}$, which was in turn time-consuming and laborious, due to their low SRP concentrations, the water sampling was conducted over two periods as described above. River water samples were transported to the laboratory and filtered through glass fiber filters with a nominal pore size of 0.8 µm (GA-200, Advantec) immediately after collection and then stored at the temperature of 4 ℃ in the dark until analysis.

Additionally, we collected samples regarded as potential sources of PO_4^{3-} for waterways, i.e., fertilizer, sewage treatment water, paddy field soil, and bedrock. Manufactured organic and chemical fertilizers were provided from a distributing company and farmers and contained 8% and 28% P, respectively (Ishida et al. 2019). Because the same kinds of fertilizers are used throughout Shiga Prefecture, the $\delta^{18}O_{PO_4}$ in the fertilizers provided was used for data analysis in both Ado River and Yasu River. Sewage treatment water (4–5 L) was directly sampled with a plastic bucket from final storage pools of the wastewater treatment plants in the rural areas of the two river watersheds. Paddy field soils were sampled from a depth of about 10 cm corresponding to the upper root layer at the center of two sites in the Yasu River watershed (Fig. 1). For bedrock samples, gravels were collected from the riverbed in tributaries draining area covered by a single bedrock type, while clay was collected from an outcrop at a fault to represent the sedimentary rock end-member (Fig. S1). Riverbed gravel was assumed to be better representatives of the rocks in each draining area of the tributaries than the bedrock because they are flowed from the whole drainage area to the outlet and thus encompass the bedrock heterogeneity. The clay was sampled at just one site in this study because other rock exposures were not available.

Fertilizers were dried at 50 ℃, ground to a powder with a Multi-Beads Shocker (YASUI KIKAI), and then 2–6 g of it was shaken with 100-mL ultrapure water for an hour to extract labile PO_4^{3-}. Paddy field soils were air-dried, sieved through a 2-mm mesh, and then shaken with a 0.5-M sodium bicarbonate solution to extract labile PO_4^{3-}. Bedrock samples were washed with ultrapure water, dried at 50 ℃, ground to a powder, and then about 3 g of it was immersed into 200 mL of a 1-M hydrochloric acid for 16 h to extract inorganic P. Samples preparation and analysis are detailed in Ishida et al. (2019).

Chemical and data analyses

SRP concentrations in river water samples were measured using the molybdenum blue spectrophotometric method (Multiskan™ GO Microplate Spectrophotometer, Thermo Fisher Scientific Inc.). The $\delta^{18}O_{PO4}$ in each sample was prepared and measured following a procedure modified from McLaughlin et al. (2004). Briefly, magnesium-induced co-precipitation (MagIC) was used to extract PO_4^{3-} as brucite from each sample solution. We used magnesium chloride and sodium hydroxide to settle brucite floc at a pH ranging from 10.5 to 11.5 in the solution. The settled brucite floc was centrifuged, extracted from the solution, and dissolved using concentrated acetic acid and 10-M nitric acid. Then, the dissolved brucite was passed through the solid phase extraction cartridge (Oasis HLB columns, Waters Corp.; Inertsep PLS-3 columns, GL Sciences Inc.) to remove

organic matters, and subsequently the solution was buffered at pH 5.5 with a 1-M potassium acetate. After that, each sample was processed, following McLaughlin et al. (2004). Isotopic analyses were conducted using a thermal conversion elemental analyzer–isotope ratio mass spectrometer (Delta plus XP via ConFlo III, Thermo Fisher Scientific Inc.) as presented in Ishida et al. (2019). The oxygen isotope ratio of water $\left(\delta^{18}O_{H_2O}\right)$ in river water samples was measured using cavity ring-down spectroscopy (L2120-I, Picarro) with an analytical precision of 0.05‰. Dissolved silica (SiO_2) concentrations in river water samples of Yasu River were also measured using the molybdenum yellow method (Multiskan™ GO Microplate Spectrophotometer, Thermo Fisher Scientific Inc.).

To examine whether the observed $\delta^{18}O_{PO_4}$ in river water reached isotope exchange equilibrium by biological mediation that exchanges O in PO_4^{3-} with ambient water at the temperature of reaction, the $\delta^{18}O_{PO_4}$ expected from complete isotope exchange equilibrium $\left(\delta^{18}O_{PO_4\,Eq}\right)$ was calculated by the following equation developed by Longinelli and Nuti (1973):

$$\delta^{18}O_{PO_4\,Eq} = 25.9 - T/4.3 + \delta^{18}O_{H_2O} \quad (1)$$

where T is the ambient temperature (℃) and $\delta^{18}O_{H_2O}$ is the oxygen isotope ratio of the ambient water (‰). While there are other equations published (e.g., Chang and Blake 2015) we chose this one because it has been the one most widely used and hence allows for a better comparison to other studies.

SRP concentrations and the $\delta^{18}O_{PO_4}$ were compared between Ado River and Yasu River using the Mann–Whitney U test. Variabilities were also compared between the two rivers using a test for the equality of variances. Tukey–Kramer tests were used to compare the mean values of $\delta^{18}O_{PO_4}$ among potential sources of PO_4^{3-} in each of the two rivers. Normality (Shapiro–Wilk test) and homogeneity (Bartlett test) were verified in advance. To examine whether $\delta^{18}O_{PO_4}$ in river water could be explained by land cover or geology, regression models were applied to the relationships between the $\delta^{18}O_{PO_4}$ and land or bedrock coverage. We used a geographic information system (ArcGIS 10.2; ESRI Japan) to determine land cover and lithological type in the Ado River and the Yasu River watersheds, based on 1/50,000 digitized vegetation map obtained from the Biodiversity Center of Japan and 1/200,000 digital geological map published by the Geological Survey of Japan. We then calculated the areal proportion of land or bedrock cover in each drainage of the river sampling sites for the $\delta^{18}O_{PO_4}$. Since water samples were collected at two different times in Ado River, the relationships between the $\delta^{18}O_{PO_4}$ and land or bedrock coverage were explored with a linear-mixed effects (LME) model, in which the timing of water sampling was treated as a random effect. An analysis of covariance (ANCOVA) was used to examine whether the relationships between the $\delta^{18}O_{PO_4}$ and land or bedrock coverage were different between the two rivers. Furthermore, residuals of the regression models were calculated to evaluate the extent to which land cover or geology could not explain variations in river $\delta^{18}O_{PO_4}$ as follows:

$$y - \hat{Y} = \delta^{18}O_{PO_4} - \left(b_0 - b_1 x\right) \quad (2)$$

where y is the observed $\delta^{18}O_{PO4}$ (‰), $\hat{Y}$ is the $\delta^{18}O_{PO_4}$ estimated by the best-fitting regression model between $\delta^{18}O_{PO_4}$ and land or bedrock coverage, b_0 and b_1 are the empirical parameters, and x is the land or bedrock coverage within a river drainage, such as, paddy field coverage, sedimentary rock coverage, and accretionary complex coverage. Then, we examined the relationship between the residuals and the drainage area in the river sampling sites. We used the determination coefficient to select the best-fitting regression model when estimating $\hat{Y}$.

Results

SRP concentrations were lower in Ado River than in Yasu River on average (Fig. 2a), though the difference was not statistically significant (U-test, $p = 0.105$). Variability of SRP concentrations was significantly lower in Ado River than in Yasu River (test for the equality of variances, $p < 0.001$). The $\delta^{18}O_{PO_4}$ in Ado River and Yasu River was 19.0 ± 2.4‰ ($n = 7$) and 13.1 ± 2.3‰ ($n = 15$) on average, respectively. These ratios were significantly different from each other (U test, $p < 0.001$; Fig. 2b). On the other hand, the variability in the $\delta^{18}O_{PO_4}$ values was not significantly different (test for the equality of variances, $p > 0.05$). The $\delta^{18}O_{PO_4}$ was more positive in Ado River (19.7 ± 2.5‰) than in Yasu River (11.5 ± 1.2‰) when the data of river drainages with forest coverage of more than 70% are compared (U-test, $p < 0.01$; Fig. 2c). The measured $\delta^{18}O_{PO_4}$ deviated from the value expected for complete isotope exchange equilibrium $\left(\delta^{18}O_{PO_4\,Eq}\right)$ in both Ado River and Yasu River (Fig. 3). There were no significant correlations between SRP concentrations and the $\delta^{18}O_{PO_4}$ in Ado River ($r = -0.30$, $p = 0.507$) and Yasu River ($r = -0.06$, $p = 0.840$).

In Ado River, the $\delta^{18}O_{PO_4}$ (19.0 ± 2.4‰) was similar to that in rocks from the accretionary complex (17.5 ± 2.9‰), but significantly different from those in fertilizer (14.3 ± 2.5‰) and sewage treatment water (14.8 ± 1.2‰) (Tukey–Kramer, $p < 0.05$; Fig. 4). In Yasu River, the range of the $\delta^{18}O_{PO_4}$ values (10.3–17.6‰) overlapped with several potential sources of PO_4^{3-}, such as, fertilizer (12.7–17.2‰), sewage treatment water (14.0–15.9‰), granite and accretionary complex rocks (11.0–13.4‰) (Fig. 4). There was a strong correlation between the

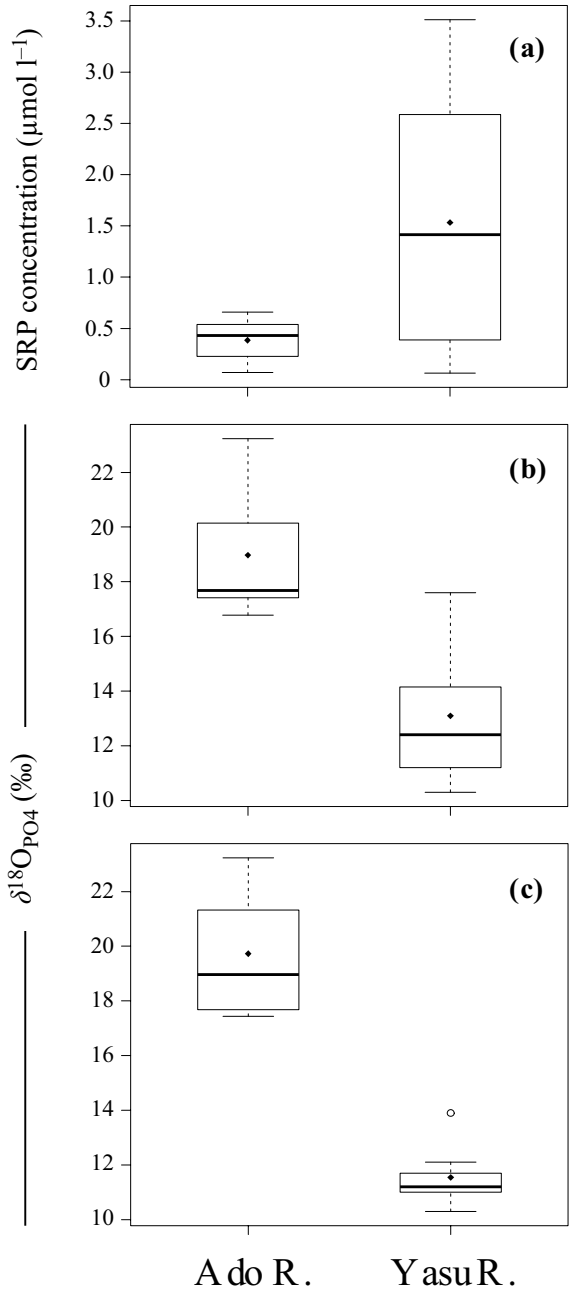

Fig. 2 **a** Boxplot for soluble reactive phosphorus (SRP) concentration and **b**, **c** $\delta^{18}O_{PO4}$ in Ado River and Yasu River. **c** represents data obtained in river drainages where more than 70% of land cover is occupied by forest. Closed diamond and open circle in the figure represent mean and outlier values, respectively

$\delta^{18}O_{PO_4}$ values in river water and rocks, i.e., accretionary complex, granite and sedimentary rocks ($r = 0.95$, $p < 0.05$; Fig. 5a). Additionally, in the river drainages with forest coverage of more than 70%, the $\delta^{18}O_{PO_4}$ in river water tended to be almost the same as that in rocks from the accretionary complex (Fig. 5b).

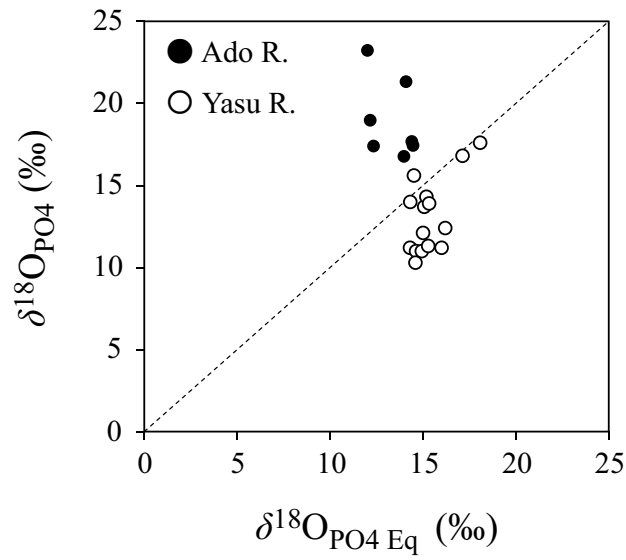

Fig. 3 Relationship between the measured and the calculated $\delta^{18}O_{PO_4}$ values by the equation of isotope exchange equilibrium $(\delta^{18}O_{PO_4\,Eq.})$, i.e., Eq. (1), in Ado River and Yasu River

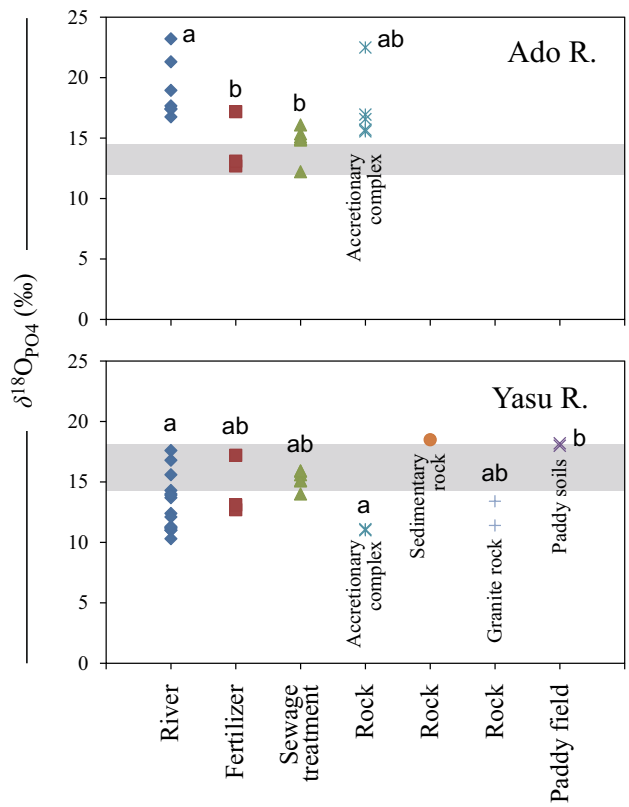

Fig. 4 The $\delta^{18}O_{PO_4}$ of river water and potential PO_4^{3-} sources in Ado River and Yasu River. Values with the same alphabetical letter indicate no significant difference ($p > 0.05$). The gray zone in the figure indicates the range of the calculated $\delta^{18}O_{PO_4}$ values by the equation of isotope exchange equilibrium $(\delta^{18}O_{PO_4\,Eq.})$, i.e., Eq. (1) in the river water

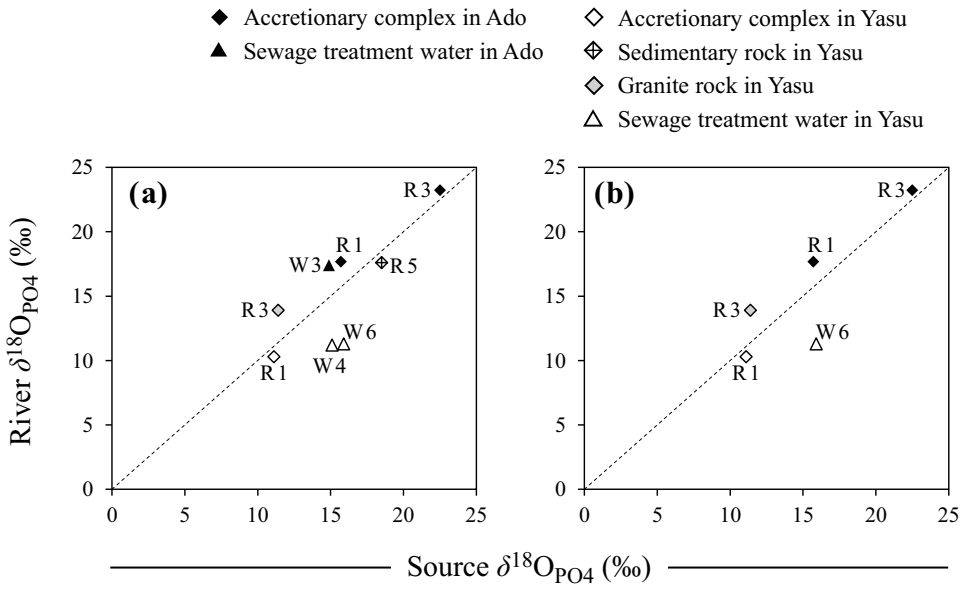

Fig. 5 **a** Relationships between the $\delta^{18}O_{PO_4}$ of river water and potential PO_4^{3-} sources in seven and **b** four rivers within the Ado River and the Yasu River systems. Forests account for more than 70% of the four river drainages in **b**. The ID number of each potential PO_4^{3-} source in the figure corresponds to that in Fig. 1 and Table S3. Note that in the upper reach of Ado River system, river water 1 was assumed to belong to the drainage with accretionary complex R1 (Figs. 1 and S1)

In Ado River, while the $\delta^{18}O_{PO_4}$ tended to increase with accretionary complex coverage in the drainage (Fig. 6b, c; test for the significance of the regression, $p > 0.05$), it decreased with increasing sedimentary rock coverage (test for the significance of the regression, $p < 0.05$). In Yasu River, the $\delta^{18}O_{PO_4}$ significantly increased with the paddy field or the sedimentary rock coverage in a drainage, but decreased with increasing accretionary complex coverage (Fig. 6d–f; test for the significance of the regression, $p < 0.05$ in all cases). There were significant correlations ($p < 0.05$) between the paddy field, sedimentary rock, and accretionary complex coverage (Table S1). The variability in the $\delta^{18}O_{PO_4}$ values could be better explained by the relative extent of the paddy field cover than by any other category of land cover and geology in the drainage. The relationship between the $\delta^{18}O_{PO_4}$ and land or bedrock coverage significantly differed between Ado River and Yasu River (ANCOVA, $p < 0.01$ in all cases in Fig. 6).

The $\delta^{18}O_{PO_4}$ in river water appeared to approach a constant value as the drainage area increased (Fig. 7a). When residuals were calculated using the best-fitting regression model between $\delta^{18}O_{PO_4}$ and land or bedrock coverage in Ado River and Yasu River (Fig. 6c, d) and then plotted against the drainage area (Fig. 7b), the variability tended to become smaller as the drainage area increased. A similar pattern was found in dissolved silica (SiO_2) concentrations obtained in the Yasu River system (Fig. 8). Bin-averages of SiO_2 concentrations separated by the drainage area were similar on a logarithmic scale from drainage areas of 10^{-1} to 10^3 km^2. However, their standard deviations significantly ($p < 0.05$) decreased with increasing drainage area.

The $\delta^{18}O_{PO_4}$ at the outlet of the Yasu River watershed was similar to the $\delta^{18}O_{PO_4\,Eq}$ (Fig. 9). The $\delta^{18}O_{PO_4}$ in river water did not approach the $\delta^{18}O_{PO_4\,Eq}$ as the drainage area increased; however, the variability in the difference between $\delta^{18}O_{PO_4}$ and $\delta^{18}O_{PO_4\,Eq}$ appeared to become smaller and converge toward a constant value with increasing drainage area.

Discussion

The $\delta^{18}O_{PO_4}$ significantly differed between Ado River and Yasu River, but SRP concentrations did not significantly differ (Fig. 2a, b). The variability in the $\delta^{18}O_{PO_4}$ was similar between the two rivers, whereas the variability in SRP concentrations was significantly larger in Yasu River than in Ado River, indicating that the SPR concentration reflects larger variations in land-cover and geological compositions in the Yasu River watershed than in the Ado River watershed. Comparisons between the $\delta^{18}O_{PO_4}$ in river water and potential sources of PO_4^{3-} revealed that in Ado River, the $\delta^{18}O_{PO_4}$ was similar to that in rocks from the accretionary complex (Figs. 4, 5). Additionally, a significant negative relationship between the $\delta^{18}O_{PO_4}$ and sedimentary rock coverage (Fig. 6) indicates that the $\delta^{18}O_{PO_4}$ is related to geological substances in the Ado River watershed. The sedimentary rocks cover relatively flat lands in the lower watershed while the accretionary complexes occupy forest areas within the mountainous terrain (Fig. S1; Crook et al. 2018; Ishii and Takahashi 1993; Isozaki 1997; Taira 2001). The $\delta^{18}O_{PO_4}$ increase seen with the accretionary complex coverage in the Ado River watershed suggests that PO_4^{3-} in river water derives mainly from the weathering of bedrock in this watershed (Hypothesis 1). Jaisi and Blake (2010) measured the $\delta^{18}O_{PO_4}$ in continental margin sediments collected along the Peru Margin and

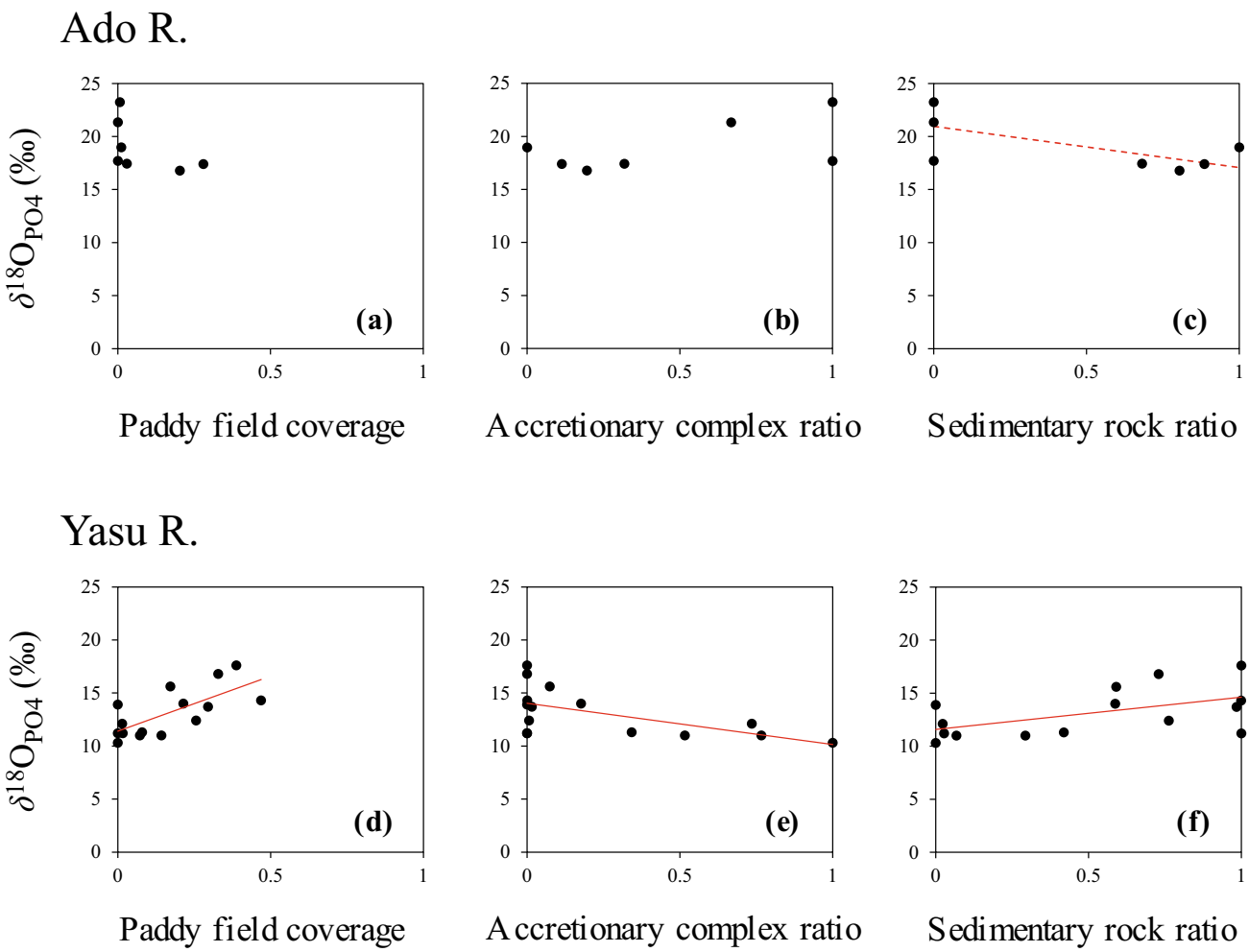

Fig. 6 Relationships between river $\delta^{18}O_{PO_4}$ and paddy field coverage or bedrock (i.e., accretionary complex and sedimentary rocks) coverage in river drainages of the Ado River and the Yasu River systems. Broken and solid lines represent the linear mixed-effects model (**c** $y=-3.88x+20.96$, $R^2=0.55$) and the regression line without a random effect (**d** $y=10.37x+11.40$, $R^2=0.51$; **e** $y=-3.88x+14.03$, $R^2=0.51$; **f** $y=3.04x+11.58$, $R^2=0.30$), respectively

showed that authigenic phosphate had $\delta^{18}O_{PO_4}$ values from 20.2 to 24.8‰. They suggested that in marine sediments, authigenic apatite precipitated at/near the sediment–water interface, in equilibrium with the oxygen isotope ratios of the porewater at the time and the paleoenvironmental temperature of precipitation. Because most of the accretionary wedge in our study site consists of marine sediments with biogenic marine apatite and only small amounts of igneous apatite (Isozaki et al. 1990), rocks from the accretionary complex would have high $\delta^{18}O_{PO_4}$. This may explain the higher $\delta^{18}O_{PO_4}$ in Ado River than in Yasu River (Fig. 2), because the dominant bedrock type in the Ado River watershed is the accretionary complex. In addition to the weathering of bedrock, PO_4^{3-} derived from forest soils might have affected the $\delta^{18}O_{PO_4}$ in Ado River, though we did not measure the $\delta^{18}O_{PO_4}$ in forest soils due to the difficulty in analyzing the forest-soil $\delta^{18}O_{PO_4}$ (Ishida et al. 2019). Several studies have suggested that the $\delta^{18}O_{PO_4}$ values of labile and less labile P fractions in soil samples are close to the $\delta^{18}O_{PO_4\,Eq}$ and rock-derived $\delta^{18}O_{PO_4}$ values, respectively, in natural ecosystems (Angert et al., 2012; Roberts et al., 2015; Tamburini et al. 2012). If this is the case with our study, the $\delta^{18}O_{PO_4\,Eq}$ of labile P fractions in forest soils is predicted to range from 12.0 to 14.5‰ based on the $\delta^{18}O_{H_2O}$ and water temperature in rivers with forest coverage of more than 70%, and is much lower than those of the $\delta^{18}O_{PO_4}$ in the Ado River and rock samples (Tables S2, S3).

The overlap between the $\delta^{18}O_{PO_4}$ in river water and potential sources in the Yasu River watershed indicates that it is impossible to determine the exact dominant source of PO_4^{3-} in river water using the $\delta^{18}O_{PO_4}$ alone. However, a

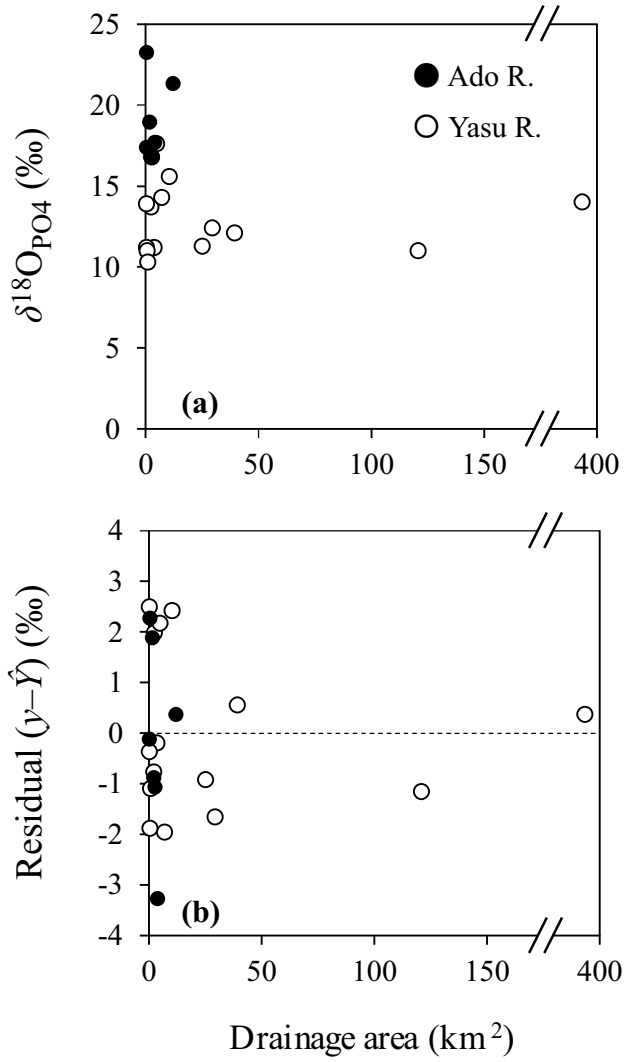

Fig. 7 **a** Relationships between the river $\delta^{18}O_{PO_4}$ and the drainage area and **b** between residuals of regression equations of the river $\delta^{18}O_{PO_4}$ and paddy field or sedimentary rock coverage and the drainage area

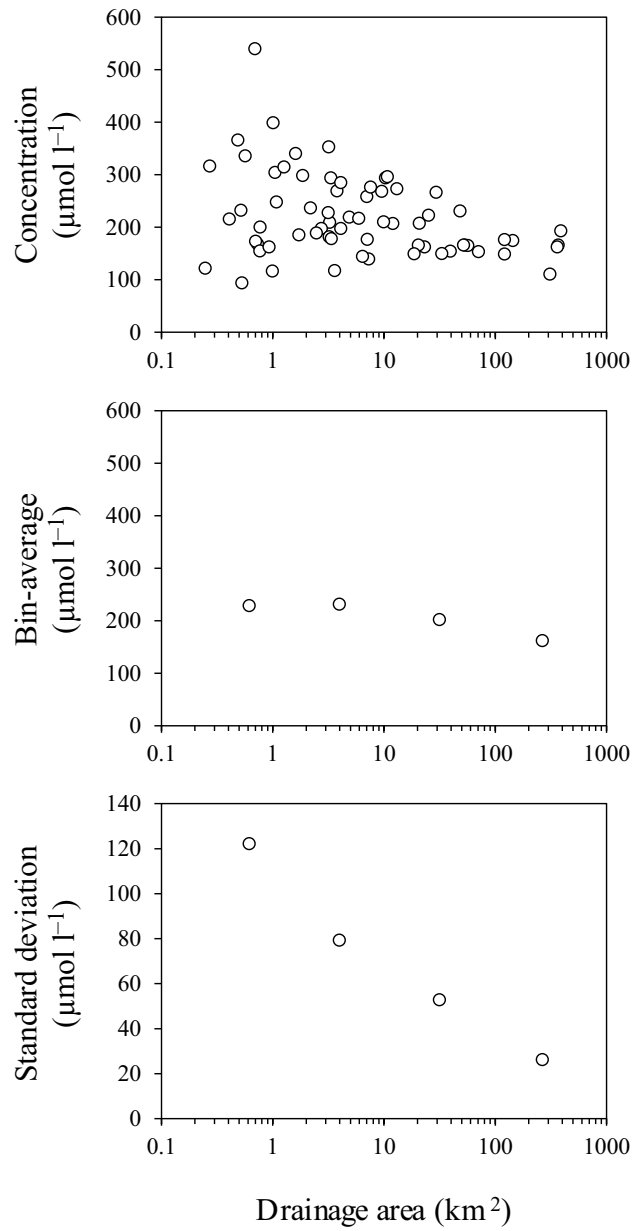

Fig. 8 Relationship between the SiO_2 concentration and the drainage area within the Yasu River system. Bin-averages and standard deviations were calculated using data separated by the drainage area on a logarithmic scale

significant strong relationship between the $\delta^{18}O_{PO_4}$ in river water and paddy field coverage in the Yasu River watershed (Fig. 6) indicates that the $\delta^{18}O_{PO_4}$ is related to land cover. Since the $\delta^{18}O_{PO_4}$ in paddy field soils presented a value of 18‰ which is higher than that of the bedrock in the upper watershed (i.e., accretionary complex and granite rock; Figs. 4, S1), the result suggests that the transport of PO_4^{3-} from the paddy fields to the river increases the $\delta^{18}O_{PO_4}$. The $\delta^{18}O_{PO_4}$ in paddy field soils is attributable to the fact that the $\delta^{18}O_{PO_4}$ of added PO_4^{3-} from the fertilizer used is rapidly driven towards isotopic equilibrium with soil water via microbial enzymatic activity (Gross and Angert 2015; Ishida et al. 2019; Jaisi et al. 2011; Tamburini et al. 2012; Zohar et al. 2010). Because paddy fields can temporarily retain water due to the low-permeable subsoil, oxygen isotopes of added PO_4^{3-} as fertilizer are expected to be easily exchanged with those of soil water. The $\delta^{18}O_{PO_4}$ in paddy field soils was similar to that in sedimentary rocks (Fig. 4). This is attributable to the fact that sedimentary rock also contains biogenic apatite and thus have a high $\delta^{18}O_{PO_4}$ (Crook et al. 2018; Longinelli and Nuti 1973). Since sedimentary rocks are distributed in the middle and lower reaches of the Yasu River watershed as well as paddy fields (Figs. 1, S1), it is possible that the transport of PO_4^{3-} from

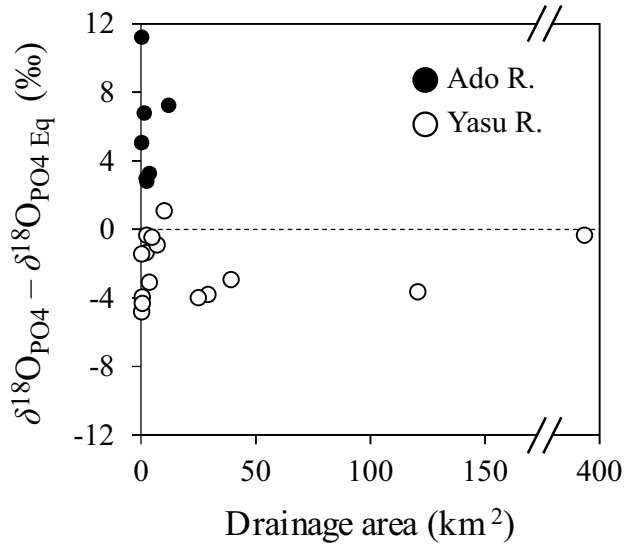

Fig. 9 Relationship of differences between the measured and the calculated $\delta^{18}O_{PO_4}$ values by Eq. (1) to the drainage area in Ado River and Yasu River

the sedimentary rocks to the river increases the $\delta^{18}O_{PO_4}$. On the other hand, the $\delta^{18}O_{PO_4}$ in sedimentary apatite can vary greatly depending on rock age and location (Kolodny et al. 1983; Longinelli and Nuti 1973).

While the $\delta^{18}O_{PO_4}$ increased with increasing paddy field coverage in Yasu River, it tended to decrease in Ado River (Fig. 6a, d). Additionally, it increased with sedimentary rock coverage in Yasu River, but decreased in Ado River (Fig. 6c, f). These results demonstrate that the $\delta^{18}O_{PO_4}$ in river water reflects inputs from geological substances and is impacted by land-use activities, but the relationship between the $\delta^{18}O_{PO_4}$ and land cover or geology is distinct to each watershed (Hypothesis 2). The river $\delta^{18}O_{PO_4}$ in upstream forest areas would often reflect bedrock PO_4^{3-} because of limited anthropogenic P sources. While the $\delta^{18}O_{PO_4}$ was relatively low in the forest areas of Yasu River, it was high in Ado River probably due to the contribution of the high $\delta^{18}O_{PO_4}$ from the accretionary complex rock (Figs. 2c, 4, and 5). The bedrock-derived $\delta^{18}O_{PO_4}$ in river water should change as water flows downstream due to the supply of PO_4^{3-} from several anthropogenic P sources to the river, which in turn causes differences in the relationship of the $\delta^{18}O_{PO_4}$ to anthropogenic land coverage, such as, paddy field coverage, between Ado River and Yasu River. In Yasu River, the supply of PO_4^{3-} from paddy fields would increase the $\delta^{18}O_{PO_4}$, but in Ado River, it would decrease the $\delta^{18}O_{PO_4}$ because of the higher $\delta^{18}O_{PO_4}$ in the bedrock than in the paddy fields. This is also supported by the higher values of the $\delta^{18}O_{PO_4}$ in Ado River than in Yasu River, where paddy field are not present (Fig. 6a, d). Our results, therefore, suggest that geology is a primary factor characterizing the $\delta^{18}O_{PO_4}$ in pristine river water, which subsequently varies depending on inputs from anthropogenic sources of phosphate as the water flows downstream. A few studies have investigated the relationship between the $\delta^{18}O_{PO_4}$ in river water and potential sources and concluded that $\delta^{18}O_{PO_4}$ can be used as a tracer of PO_4^{3-} within a river system as long as the potential sources are isotopically distinct and biological phosphate cycling is low (Gooddy et al 2018; Granger et al. 2017; Tonderski et al. 2017; Young et al. 2009). However, no study has systematically measured the $\delta^{18}O_{PO_4}$ of river water and potential sources, including several bedrock types, from pristine rivers to human-impacted rivers within a watershed to examine whether the relationship is consistent between different watersheds. Our results demonstrated differences in the relationship of land or bedrock coverage to river $\delta^{18}O_{PO_4}$ between nearby watersheds under the same climate.

The relationship of the residuals of the regression models between river $\delta^{18}O_{PO_4}$ and land or bedrock coverage to the drainage area (Fig. 7) indicates that while residuals exhibited large variability in a smaller drainage area, they tended to converge toward a constant value, i.e., zero, as the drainage area increased. This might be attributed to the fact that the spatial variability in the hydrology in a watershed decreases with increasing watershed area, due to the mixing and integration of many small-scale hydrological conditions (Wood et al. 1988; Sivapalan et al. 2002; Asano et al. 2009). Asano et al. (2009) and Asano and Uchida (2010) investigated the concentration spatial patterns of dissolved silica (SiO_2) in the steep headwaters of a 4.27 km^2 watershed within the Lake Biwa basin, and found a convergent relationship between stream SiO_2 concentration and drainage area. Based on the convergent relationship, Uchida and Asano (2010) indicated that streamflow of first- to sixth-order streams consisted of water flowing through the soil layer and emerging from bedrock groundwater, and the mixing ratio of water from those sources converged towards a constant as the drainage area and stream order increased. Some studies have noted that hydrological processes within a 1-km^2 drainage area are governed by hillslope processes related to soil depth, topography and vegetation (Gomi et al. 2002; Wood et al. 1988; Woods et al. 1995), which result in great variations in unit area discharge and element concentrations. In contrast, hydrologic responses in drainages greater than 1 km^2 are more affected by routing processes, in which tributary outflows from numerous nested headwaters join together into downstream rivers and several hydrologic responses can be averaged. Our result (Fig. 8) exhibited a convergent pattern of SiO_2 concentration with an increase in drainage area. Given that the $\delta^{18}O_{PO_4}$ is different between water from the soil layer and the bedrock groundwater, the $\delta^{18}O_{PO_4}$ in river water should be affected by the drainage area via differences in flowpaths contributing to the river.

Therefore, the convergent relationship between the residuals and the drainage area (Fig. 7) suggests that the mixing ratio of soil-derived and bedrock-derived $\delta^{18}O_{PO_4}$ in river water converges toward a constant as drainage area increases, whereas it varies in a small drainage area, which causes large variability in part of the $\delta^{18}O_{PO_4}$ that could not be explained by land cover and geology (Hypothesis 3). It is possible that $\delta^{18}O_{PO_4}$ in river water is better explained by land cover and geology on a larger watershed scale.

Another possible explanation for the convergent pattern of residuals is an increase in the frequency of biologically mediated oxygen isotope exchange between river PO_4^{3-} and ambient water with increasing drainage area. The phosphorus–oxygen (P–O) bond in PO_4^{3-} is resistant to inorganic hydrolysis and PO_4^{3-} does not exchange oxygen with ambient water at the temperature and pH of most natural systems (Blake et al. 1997; Longinelli et al. 1976; O'Neil et al. 2003). However, the P–O bond can be easily broken in enzyme-mediated biochemical reactions (Dahms and Boyer 1973; Boyer 1978). Because river length increases with drainage area, it is plausible that opportunities for biological uptake of PO_4^{3-} in river water increase as the drainage area and the transit time of water through a river increases, which in turn promotes enzyme-mediated biochemical reactions and consequently oxygen isotope exchange, and thus resets the isotopic signature primarily to a temperature-dependent equilibrium value (Blake et al. 2005; Paytan et al. 2002; Paytan and McLaughlin 2007). This also would be supported by a convergent pattern of the variability in the difference between $\delta^{18}O_{PO_4}$ and $\delta^{18}O_{PO_4\,Eq}$ (Fig. 9). However, not all PO_4^{3-} is fully cycled and the cycled PO_4^{3-} is mixed with anthropogenic and/or geological derived PO_4^{3-} within a river (McLaughlin et al., 2006c). This indicates that the $\delta^{18}O_{PO_4}$ could preserve the signatures of anthropogenic and geological P sources even in the downstream rivers with large drainage area. Therefore, the convergent pattern of residuals implies that part of the $\delta^{18}O_{PO_4}$ value, which could not be explained by land cover and geology, approaches a constant value that reflects isotopic equilibrium as the water flows downstream.

Conclusion

This study sought to clarify what factors characterize $\delta^{18}O_{PO_4}$ in river water by comparing the $\delta^{18}O_{PO_4}$ between two rivers, Ado River and Yasu River, and between the rivers and potential sources of PO_4^{3-}. Our results demonstrate that $\delta^{18}O_{PO_4}$ in river water strongly reflects inputs from geological substances in pristine environments and subsequently varies depending on land-use activities as the water flows downstream. Thus, the relationship between the $\delta^{18}O_{PO_4}$ and land or bedrock coverage is distinct to each river. The $\delta^{18}O_{PO_4}$ in rivers draining forests reflected bedrock-derived $\delta^{18}O_{PO_4}$, and clearly differed between the two rivers, reflecting the distinct bedrock coverage in each river watershed. This emphasizes an importance of measuring $\delta^{18}O_{PO_4}$ in rivers without anthropogenic impacts, i.e., measuring the background level of $\delta^{18}O_{PO_4}$, when $\delta^{18}O_{PO_4}$ is used as a tracer of PO_4^{3-} within a watershed.

Regression analysis of the relationship between the $\delta^{18}O_{PO_4}$ and land or bedrock coverage showed that residuals of the $\delta^{18}O_{PO_4}$ tended to converge towards zero as the drainage area increases. This indicates that the river $\delta^{18}O_{PO_4}$ could be better explained by land cover and geology on a larger watershed scale.

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