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Supporting Information for

Doubled the carbon flux as a result of increased fresh submarine groundwater discharge caused by half the “normal” snowfall over the past 20 years along the mid-latitude coast of Japan

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Introduction

This document contains supplementary material to verify some of the arguments put forward in the main paper.

Text S1. Details on the study area's hydrogeological environment

In the Katakai River Alluvial fan, the main types of geological conditions are gravel and sand sediments. The hydrogeological setting of this study area has three layers: top layer is alluvium formed in the Holocene, consisting of gravel, sand, and clay layers. The thickness of the top layer from the top of the alluvial fan to the coastal line is from 20 to about 100 m, respectively. Middle layer is the deposit of the dissected fan formed in the late and middle Pleistocene. Bottom layer is the deposit of the dissected fan from the early Pleistocene. The bedrock is sandstone and mudstone (Koku-sai Kogyo Co., Ltd., 2002). In this study, all samples were collected from the top aquifer layer.

Table S1. Sampling stations in this study

Station Name	Location		Sampling Period	Ref.
	Longitude	Latitude		
S1	137.418	36.854	2001-2002 (n=5)	R2
S2	137.415	36.852	2001-2002 (n=5)	R2
S3	137.413	36.850	2001-2002 (n=5)	R2
S4	137.423	36.845	2001-2002 (n=5)	R2
S5	137.416	36.845	2001-2002 (n=5)	R2
S6	137.405	36.836	2001-2002 (n=8)	R2
S7	137.421	36.838	2001-2002 (n=5)	R2
S8	137.414	36.833	2001-2002 (n=5)	R2
S9	137.401	36.826	2001-2002 (n=5)	R2
S10	137.406	36.825	2001-2002 (n=8)	R2
S11	137.411	36.825	2001-2002 (n=5)	R2
S12	137.417	36.824	2001-2002 (n=5)	R2
S13	137.413	36.821	2001-2002 (n=5)	R2
S14	137.406	36.821	2001-2002 (n=5)	R2
S15	137.401	36.815	2001-2002 (n=5)	R2
S16	137.410	36.816	2001-2002 (n=5)	R2
S17	137.427	36.817	2001-2002 (n=8)	R2
S18	137.433	36.820	2001-2002 (n=8)	R2
S19	137.443	36.816	2001-2002 (n=8)	R2
S20	137.432	36.810	2001-2002 (n=8)	R2
S21	137.421	36.828	2001-2002 (n=8)	R2
S22	137.402	36.837	2001-2002 (n=8), 2017-2018 (n=8)	R2 and this study
S23	137.423	36.844	2001-2002 (n=8), 2017-2018 (n=8)	R2 and this study
S24	137.440	36.819	2017-2018 (n=8)	This study
S25	137.410	36.843	2017-2018 (n=8)	This study
S26	137.419	36.821	2017-2018 (n=8)	This study
River	137.498	36.763	2001-2002 (n=8), 2017-2018 (n=6)	R2 and this study
FSGD	137.399	36.839	2000-2003 (n=16), 2018 (n=1)	R2, R3, R4, and this study
D1	137.447	36.812	2005-2015 (n=10)	R5

Table S2. The average values of δD and $\delta^{18}O$ in groundwater and river water

Station Name	2001-2002		2017-2018	
	δD	$\delta^{18}O$	δD	$\delta^{18}O$
	‰	‰	‰	‰
S1	-54.4 ± 2.7	-9.39 ± 0.16	-	-
S2	-53.8 ± 1.7	-9.45 ± 0.11	-	-
S3	-61.8 ± 3.5	-10.36 ± 0.10	-	-
S4	-61.6 ± 2.2	-10.72 ± 0.09	-	-
S5	-60.4 ± 4.1	-10.69 ± 0.06	-	-
S6	-61.9 ± 3.0	-10.53 ± 0.38	-	-
S7	-62.4 ± 4.5	-10.25 ± 0.34	-	-
S8	-59.2 ± 3.0	-10.33 ± 0.11	-	-
S9	-57.2 ± 2.5	-9.57 ± 0.38	-	-
S10	-56.9 ± 2.7	-9.79 ± 0.06	-	-
S11	-58.7 ± 3.7	-10.14 ± 0.28	-	-
S12	-56.6 ± 3.3	-10.03 ± 0.43	-	-
S13	-56.0 ± 2.9	-9.46 ± 0.07	-	-
S14	-54.1 ± 2.4	-9.43 ± 0.05	-	-
S15	-53.6 ± 5.3	-9.50 ± 0.28	-	-
S16	-56.4 ± 3.9	-9.28 ± 0.10	-	-
S17	-55.6 ± 4.4	-9.34 ± 0.12	-	-
S18	-59.6 ± 2.9	-10.12 ± 0.28	-	-
S19	-57.9 ± 3.6	-9.87 ± 0.28	-	-
S20	-55.7 ± 3.6	-9.46 ± 0.14	-	-
S21	-61.9 ± 4.8	-10.45 ± 0.46	-68.0 ± 2.3	-11.17 ± 0.36
S22	-59.0 ± 2.7	-9.92 ± 0.31	-66.3 ± 3.1	-10.81 ± 0.48
S23	-	-	-68.4 ± 3.1	-10.95 ± 0.52
S24	-	-	-65.5 ± 1.9	-10.77 ± 0.37
S25	-	-	-66.8 ± 4.5	-10.85 ± 0.53
S26	-	-	-60.5 ± 0.4	-10.13 ± 0.04
River	-62.7 ± 4.8	-10.61 ± 0.76	-68.0 ± 2.1	-10.96 ± 0.19

Table S3. Chemical and stable isotopic compositions in fresh submarine groundwater discharge (FSGD).

Sample Date	EC	pH	HCO ₃	NO ₃	PO ₄	SiO ₂	δ ¹⁸ O	δD
	mS/m		μM			‰		
2000/11/23	10.9	-	-	39	-	-	-11.0	-62.6
2002/05/28	11.3	7.38	863	41	<0.01	127	-10.7	-65.0
2002/06/26	11.3	7.19	804	41	0.04	131	-10.8	-63.5
2002/07/22	22.0	7.35	865	41	-	137	-10.7	-64.3
2003/05/28	-	-	-	43	0.09	150	-10.7	-
2003/06/03	-	-	-	44	0.08	149	-10.6	-
2003/07/09	-	-	-	46	0.05	149	-10.6	-
2003/07/29	-	-	-	44	0.03	141	-9.8	-
2003/08/07	-	-	-	44	0.04	144	-10.2	-
2003/08/21	-	-	-	44	0.03	-	-10.2	-
2003/09/07	-	-	-	43	0.02	-	-9.9	-
2003/10/07	-	-	-	37	0.09	136	-10.8	-
2003/11/04	-	-	-	47	0.06	-	-10.0	-
2003/12/10	-	-	-	46	0.04	159	-10.0	-
Average (2000-2003)	13.9 ± 5.4	7.31 ± 0.10	844 ± 35	43 ± 3	0.05 ± 0.02	142 ± 10	-10.4 ± 0.4	-63.9 ± 1.0
2018/09/17	11.7	7.32	961	29	0.03	114	-10.9	-67.0

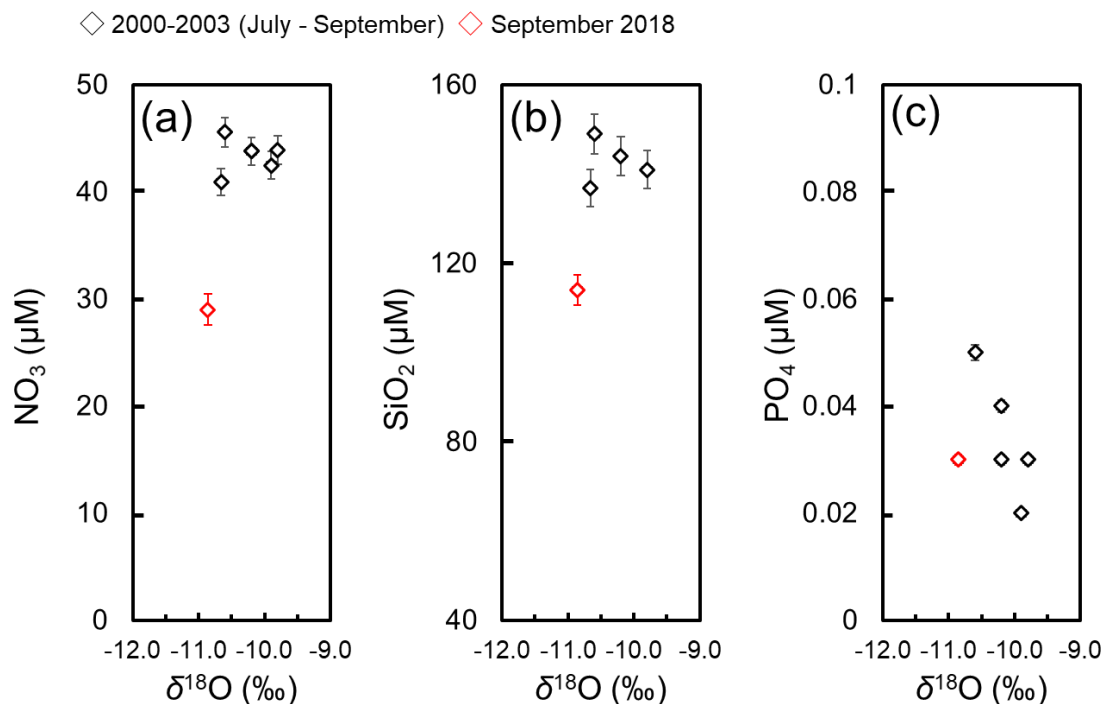


Figure S1. Relationship between $\delta^{18}\text{O}$ and (a) NO_3 , (b) SiO_2 , and (c) PO_4 in FSGD. The measurement errors are shown also. Detection limits for nutrient analysis are 0.1 $\mu\text{mol/L}$ for NO_3 , 0.1 $\mu\text{mol/L}$ for SiO_2 , and 0.01 $\mu\text{mol/L}$ for PO_4 . Black diamonds indicate previous data collected by Suzuki and Zhang (2003) and Nakaguchi et al. (2005), and red symbols show the data collected in this study (2018). Details are shown in Table S3.

Table S4. Tritium concentrations and FSGD residence time calculated from a piston flow model.

Year	^3H (TU)	Tritium Age (years)
2000	$1.1 \pm 0.2^{\text{a}}$	4 - 15 ^c (10 - 20 ^b)
2018	2.6 ± 0.1	3 - 11

Note. ^aThis sample was collected by Zhang and Satake (2003). The value at the time of sampling was 2.6 ± 0.4 TU, which was corrected to the concentration in 2018 using the half-life ($t_{1/2} = 12.32$). ^bReported Tritium age (Zhang and Satake, 2003). ^cRe-calculated Tritium age using the data (a) in this study.

Table S5. 10-year monitoring data at station D1 reported by The Water Information Database, Uozu, Toyama Prefecture, Japan.

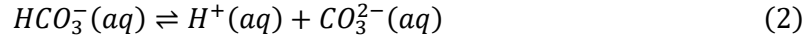
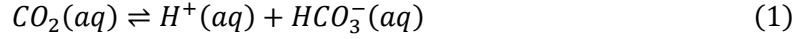
Sampling Date	2005/3/2	2006/3/2	2007/3/8	2009/3/4	2010/3/1	2011/2/22	2012/2/27	2013/2/27	2014/2/27	2015/2/25	Linear regression ^a
Water Temp. (°C)	14.0	13.8	13.2	13.5	13.1	14.0	13.0	12.7	13.2	12.9	$y = -0.0002x + 23$ ($p < 0.05$)
EC (mS/m)	12.8	13.2	12.8	11.8	12.3	11.8	13.2	12.7	13.1	12.9	$y = 0.00002x + 12$ ($p = 0.88$)
pH	7.2	7.0	7.0	6.7	6.8	6.9	6.8	6.5	6.9	6.7	$y = -0.0001x + 11$ ($p < 0.05$) ^b
DO (mg/L)	9.5	9.8	9.5	8.0	8.9	9.0	12.5	9.2	11.7	9.8	$y = 0.0004x - 6$ ($p = 0.32$)
Cl⁻ (μM)	150	178	133	116	144	124	133	121	124	93	$y = -0.014x + 676$ ($p < 0.05$) ^b
NO₃⁻ (μM)	87	97	82	56	77	48	76	71	65	50	$y = -0.009x + 434$ ($p < 0.05$) ^b
HCO₃⁻ (μM)	941	960	939	901	929	906	939	932	900	878	$y = -0.014x + 1484$ ($p < 0.05$) ^b
CO₂(aq)^c (μM)	96	156	155	294	243	184	246	492	187	291	$y = 0.053x - 1886$ ($p = 0.07$)
CO₃²⁻ ^c (μM)	3	2	2	1	1	2	1	1	2	1	$y = -0.0005x + 22$ ($p < 0.01$)
pCO₂ ^c (μatm)	2047	3303	3214	6163	5032	3929	5081	10036	3875	5977	$y = 1.06x - 37686$ ($p = 0.07$)

Note. ^aLinear regression between each chemical component (y) and sampling date (x). ^bThese lines are shown in Figure 5. ^cThese values were calculated using Text S2 and Text S3.

Text S2. Estimation of $CO_2(aq)$ and CO_3^{2-} concentrations using observation data

$CO_2(aq)$ and CO_3^{2-} concentrations were calculated using the following methods.

When H_2CO_3 is dissolved in water, an acid-base equilibrium represented by equation (1) and equation (2) is established.



The acid dissociation constant in the above acid-base equilibrium can generally be written by equation (3) and equation (4).

$$K_1 = \frac{[H^+][HCO_3^-]}{[CO_2]} \quad (3)$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad (4)$$

However, K_1 and K_2 change with water temperature (T , K), salinity (S), and water pressure. K_1 and K_2 can be determined using the following empirical formulas reported by Lueker et al. (2000).

$$pK_1 = \frac{3633.86}{T} - 61.2172 + 9.6770 \ln T - 0.011555S + 0.0001152S^2 \quad (5)$$

$$pK_2 = \frac{471.78}{T} + 25.9290 - 3.1696 \ln T - 0.01781S + 0.0001122S^2 \quad (6)$$

$$pK_n = -\log_{10} K_n \quad (7)$$

In addition, the concentration of total carbonic acid (C_T) dissolved in the aqueous solution is represented by equation (7).

$$C_T = [CO_2] + [HCO_3^-] + [CO_3^{2-}] \quad (8)$$

When equation (3) and equation (4) are transformed and substituted into equation (8), they are written as equation (9). That is, the total carbonic acid concentration (C_T) can be calculated from the water temperature (T), salinity (S), pH, and HCO_3^- concentration in each sample.

$$\begin{aligned} C_T &= \frac{[H^+][HCO_3^-]}{K_1} + [HCO_3^-] + \frac{K_2[HCO_3^-]}{[H^+]} \\ &= [HCO_3^-] \cdot \left(\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]} \right) \end{aligned} \quad (9)$$

Similarly, by deforming equation (8) and using the total carbonic acid concentration (C_T) obtained above, it is possible to finally calculate the following concentrations.

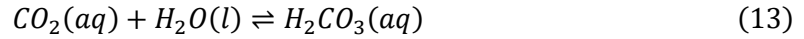
$$[CO_2] = \frac{C_T}{1 + (K_1 K_2 / [H^+]^2) + (K_2 / [H^+])} \quad (10)$$

$$[CO_3^{2-}] = \frac{C_T}{([H^+]^2 / K_1 K_2) + ([H^+] / K_2) + 1} \quad (11)$$

Text S3. Estimation of pCO_2 values using observation data

pCO_2 values were calculated using the following method.

When CO_2 is dissolved in water, it is represented by the following equations.



The equilibrium constant in equation (12) is expressed as follows.

$$K_0 = \frac{[CO_2(aq)]}{pCO_2} \quad (14)$$

$[CO_2(aq)]$ means the concentration of $CO_2(aq)$ in the aqueous solution, and pCO_2 means the partial pressure of CO_2 in the air. Equation (14) is obtained by applying Henry's law to CO_2 . The solubility under one atmosphere, expressed as K_0 , is shown as a function at water temperature (T [K]) and salinity (S) (Weiss, 1974).

$$\begin{aligned} \ln K_0 = & 93.4517 \times \frac{100}{T} - 60.2409 + 23.3685 \times \ln \frac{T}{100} \\ & + S \left\{ 0.023517 - 0.023656 \times \frac{T}{100} + 0.0047036 \times \left(\frac{T}{100} \right)^2 \right\} \end{aligned} \quad (15)$$

If CO_2 in the air dissolves in seawater (NaCl solution) and reaches the vapor-liquid equilibrium, the electrical neutrality in the seawater can be represented by equation (16).

$$[Na^+] + [H^+] = [Cl^-] + [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] \quad (16)$$

Sodium and chloride ions do not react with carbonates. That is, $[Na^+] = [Cl^-]$. When CO_2 in the air is dissolved in NaCl solution, the pH of the solution is expected to shift to acidic. Considering this, $[HCO_3^-] \gg [CO_3^{2-}]$ holds. Therefore, equation (16) can be approximated to equation (17).

$$[H^+] = [HCO_3^-] + [OH^-] \quad (17)$$

By deforming equation (17) using the ionic product of water ($K_w = [H^+] \cdot [OH^-] = 10^{-13.127}$), equation (18) is obtained.

$$[H^+] = [HCO_3^-] + \frac{K_w}{[H^+]} \quad (18)$$

By deforming equation (18) using equations (3) and (14), equation (19) is obtained, and it is finally possible to calculate the pCO_2 values.

$$[H^+]^2 = K_0 \cdot K_1 \cdot pCO_2 + K_w \quad (19)$$

Text S4. Sampling stations in river

In order to more accurately evaluate the amount of material supplied into Toyama Bay, in addition to the Katakai River Alluvial Fan, we collected samples at five river estuaries (Kurobe River, Joganji River, Jinzu River, Sho River, and Oyabe River) with large river flows. The locations are shown in Figure 1 and Table S6. These samples were collected in April, May, June, July, September, October, and November 2018. It has been reported that the water volume of these 6 rivers accounts for about 75-95% of the total river water flowing into Toyama Bay (Toyama Bay Water Conservation Study Group, 2001; Hatta et al., 2005; Hatta and Zhang, 2013). In this study, when calculating the nutrient and carbon supply in rivers in 2018, the concentrations shown in Tables S6 and S7 were used. These concentrations are weighted averages of the analyzed concentrations according to river flow.

Table S6. Water volume, pH, and chemical compositions in five rivers in 2017-2018

River	Location		Area ^a km ²	Volume ^b 10 ⁸ m ³ month ⁻¹	pH	NO ₃	PO ₄	SiO ₂	HCO ₃
	Lon.	Lat.				μM	μM	μM	mg/L
Oyabe	137.04	36.78	570	1.4±0.2	7.6	31±14	0.91±0.45	220±28	46±4
Sho	137.06	36.77	1180	1.2±0.5	7.6	15 (n=1)	0.36±0.34	143±10	29±3
Jinzu	137.22	36.75	2720	5.1±1.6	7.5	18±7	0.28±0.15	217±23	40±7
Joganji	137.28	36.73	370	0.7±0.2	7.1	13±7	0.15±0.08	194±49	30±7
Kurobe	137.43	36.92	660	1.4±1.0	7.5	11±7	0.17±0.16	125±21	22±6
5 rivers Ave.				9.9±0.2 ^c	7.5 ^d	18 ^d	0.4 ^d	193 ^d	37 ^d

Note. ^aMizutani & Satake (1997). ^bReported riverine input (Ministry of Land, Infrastructure, Transport and Tourism, Japan). ^cAveraged monthly total river flow of five rivers in 2018.

^dWeighted average concentration using river flow of each river.

Table S7. Parameters used for flux calculation

River	Water volume 10 ⁸ m ³ month ⁻¹		N-NO ₃		P-PO ₄		Si-SiO ₂		HCO ₃ ⁻		CO ₂ (aq)		CO ₃ ²⁻	
			mg/L		μg/L		mg/L		mg/L		mg/L		mg/L	
	2003	2018	2003	2018	2003	2018	2003	2018	2003	2018	2003	2018	2003	2018
FSGD	1 ^a	1.2±0.1	0.7±0.2 ^d	0.41	1.5±0.2	0.9	4.0 ^d	3.2	51.5±2.2 ^e	58.6	3.0±0.1 ^f	3.3	0.3 ^f	0.3

Note. ^aHatta & Zhang (2013). ^bYanagi et al. (2019). ^cTsujimoto et al. (2009). ^dNakaguchi et al. (2005). ^eHatta & Zhang (2013). ^fEstimated concentration from data reported by Suzuki and Zhang (2003).

Table S8. Nutrient fluxes into Toyama Bay via SGD and river water.

	N Flux (ton month ⁻¹)		P Flux (ton month ⁻¹)		Si Flux (×10 ³ ton month ⁻¹)	
	2003	2018	2003	2018	2003	2018
River	640	375 ± 100	69	18±5	5.1	8.1±2.2
FSGD	70 ± 20	48 ± 4	0.15± 0.02	0.11±0.01	0.40	0.38±0.03

Table S9. Carbon fluxes into Toyama bay via SGD and river water.

	HCO ₃ ⁻ (×10 ² ton month ⁻¹)		CO ₃ ²⁻ (×10 ² ton month ⁻¹)		CO ₂ (aq) (×10 ² ton month ⁻¹)		Total ^a (×10 ² ton month ⁻¹)	
	2003	2018	2003	2018	2003	2018	2003	2018
River	320	555 ± 150	1.6	6.0 ± 1.5	18	18 ± 5	340	580 ± 160
FSGD	52 ± 7	70 ± 30	0.3	0.4 ± 0.1	3.0 ± 1.5	4.0 ± 1.7	55 ± 9	74 ± 9

Note. ^aTotal value of three carbonate components (CO₃²⁻, HCO₃⁻, CO₂ (aq)).

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