

Supplementary Information

Andean headwater and piedmont streams are hot spots of carbon dioxide and methane emissions in the Amazon basin

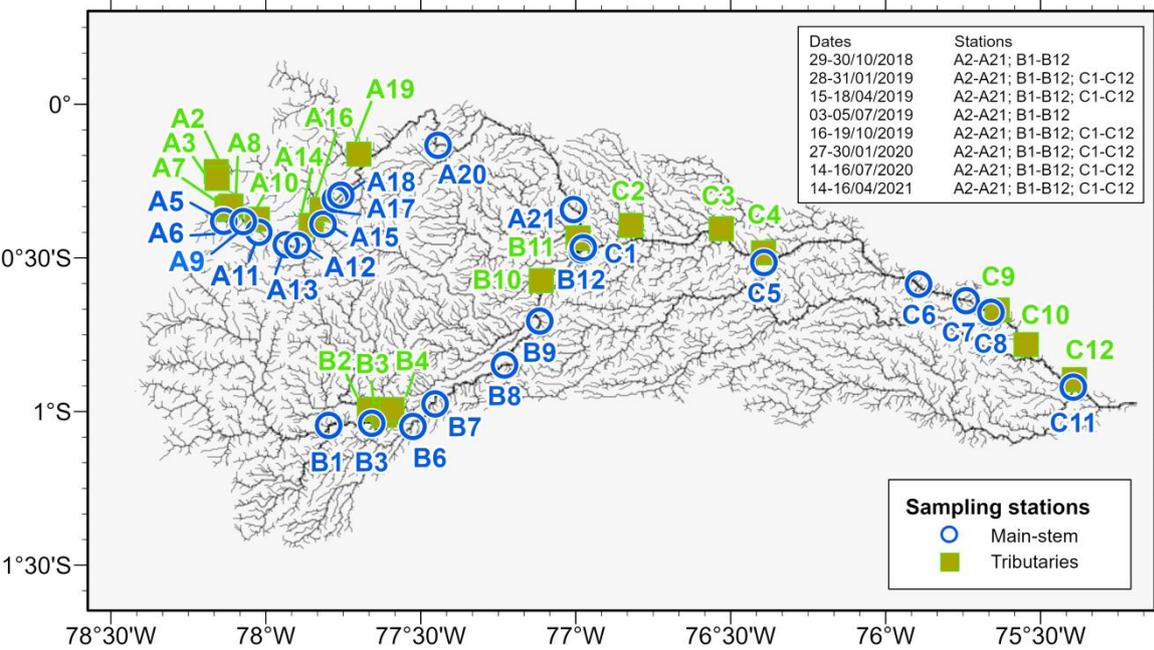
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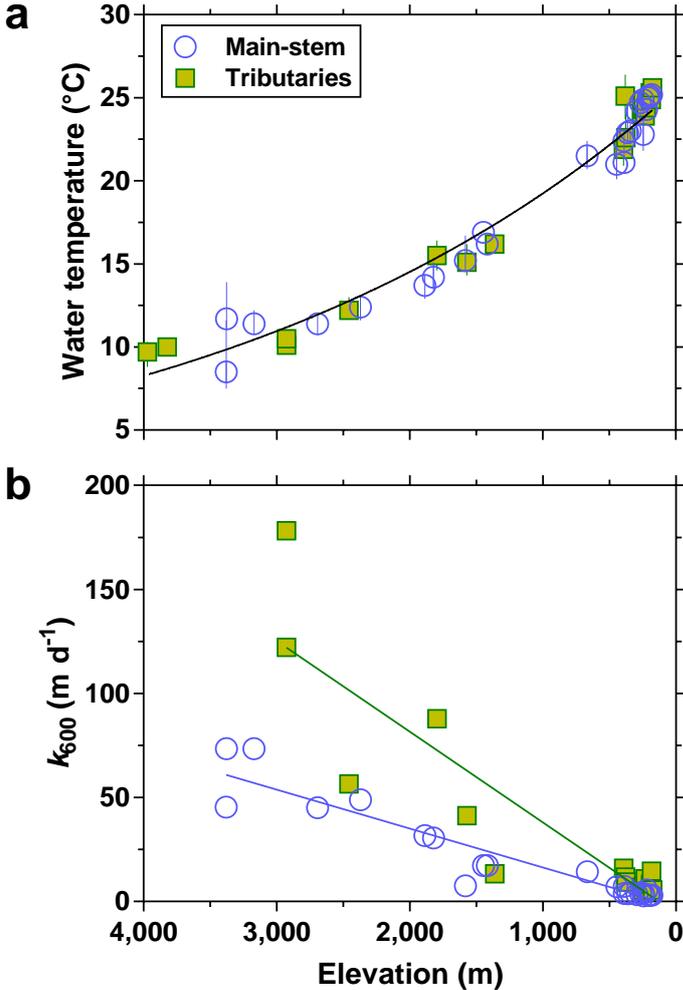
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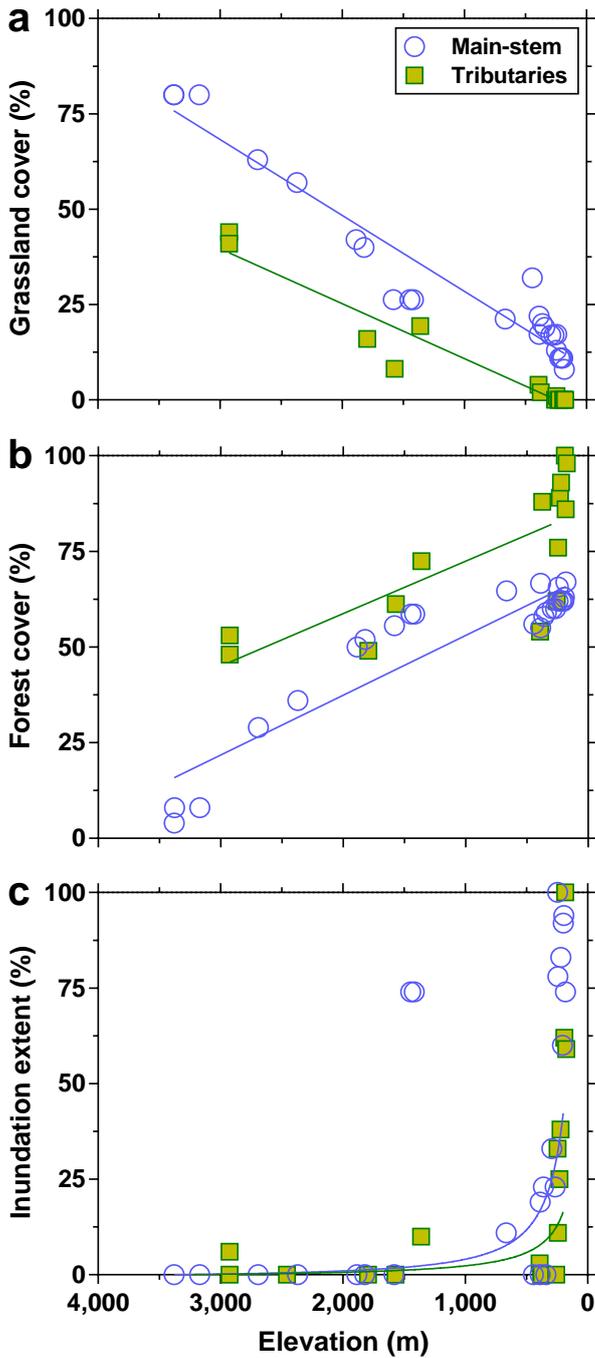
Supplementary Fig. 1 Location of stations in main-stem (blue circles) and tributaries (green squares) and sampling dates. Stations in the main-stem are shown by blue circles and in the tributaries by green squares.



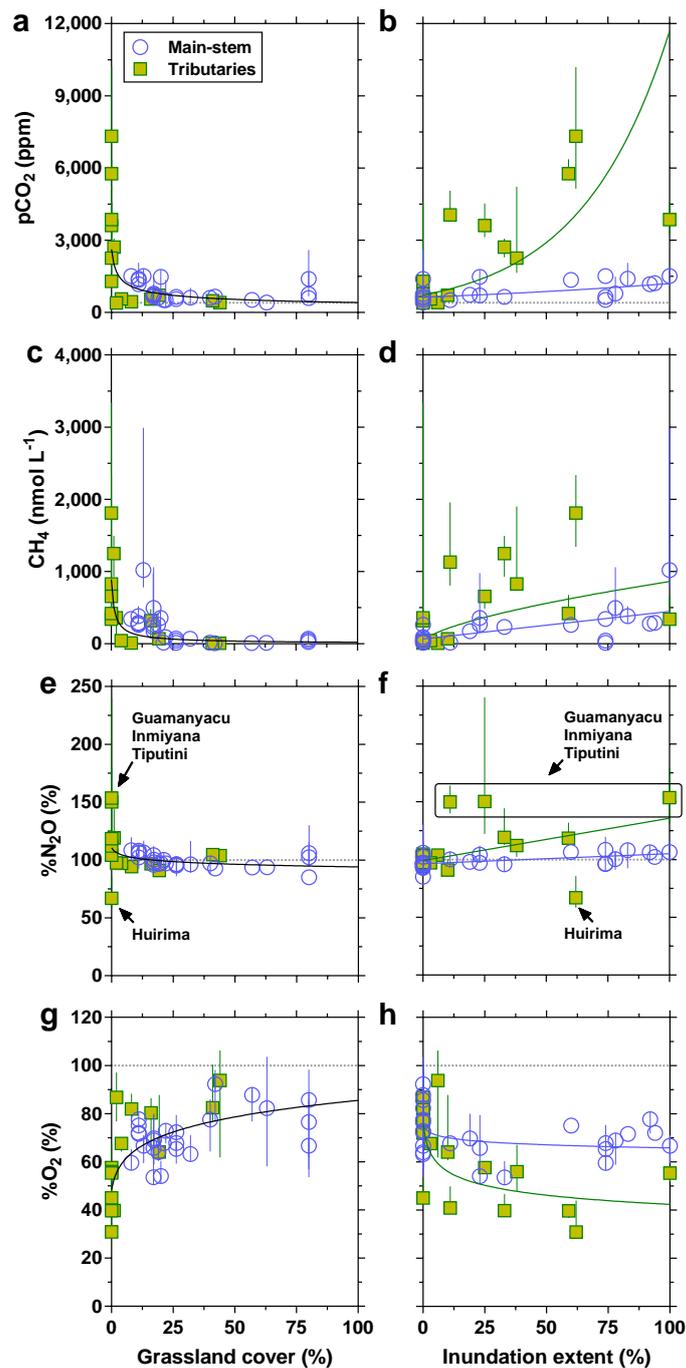
Supplementary Fig. 2 Strong elevation gradients of water temperature and gas transfer velocity in the Andean headwater and piedmont streams. Variations of measured water temperature (a) and the gas transfer velocity normalized to Schmidt number of 600 (k_{600}) modelled from freshwater discharge and stream gradient from RiverATLAS⁶⁸ (b) in the Napo streams as a function of elevation. Symbols show the median and error bars the interquartile range, stations in the main-stem are shown by blue circles and in the tributaries by green squares, and solid lines show fits to the data (Supplementary Table 4).



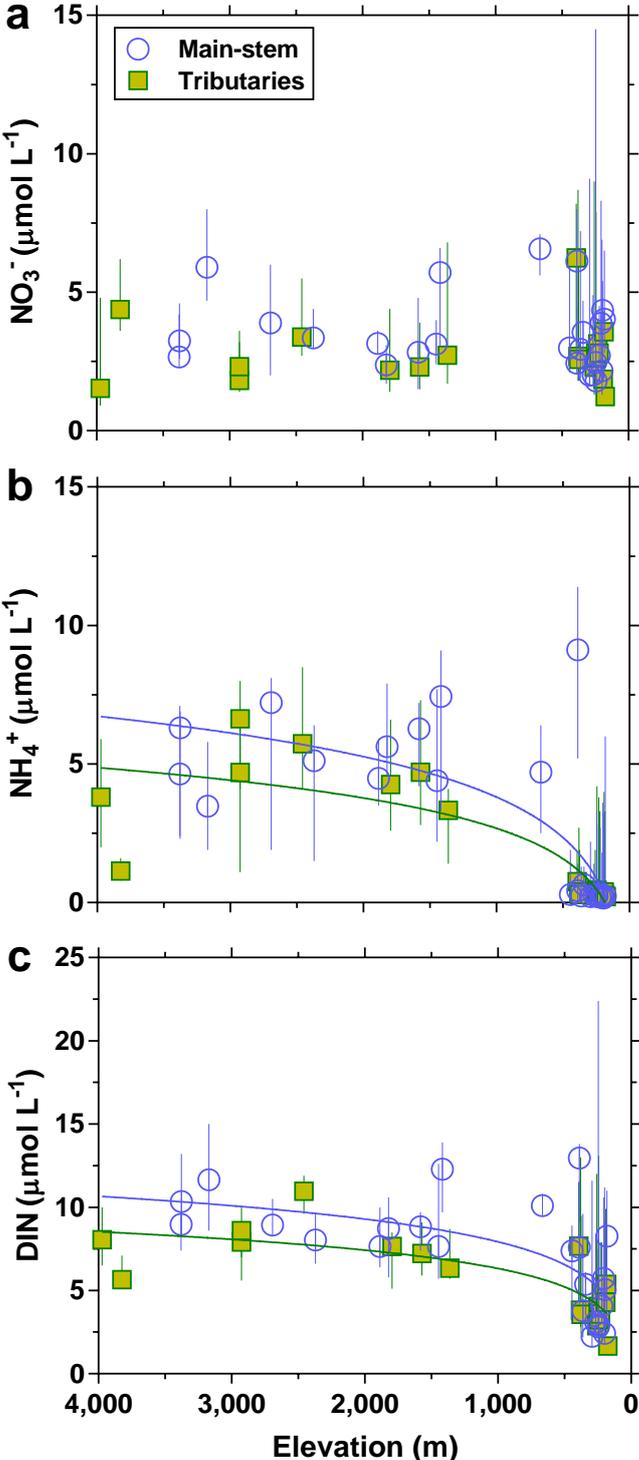
Supplementary Fig. 3 Strong elevation gradients of land cover in the catchment of Andean headwater and piedmont streams. Variations of grassland cover (a), forest cover (b) and inundation extent (c) in the Napo streams as a function of elevation, from Global Land Cover 2000¹¹⁵ and Global Inundation Extent from Multi-Satellites (GIEMS-D15)¹⁸ extracted from RiverATLAS⁶⁸. Grassland and forest cover are given over the total catchment upstream the sampled stream; inundation extent is given at the reach level. Stations in the main-stem are shown by blue circles and in the tributaries by green squares, and solid lines show fits to the data (Supplementary Table 4).



Supplementary Fig. 4 Grassland cover and inundation extent affect pCO₂, CH₄ and %N₂O in the Andean headwater and piedmont streams. Variations of the partial pressure of CO₂ (pCO₂), CH₄ dissolved concentration, N₂O saturation level (%N₂O), and oxygen saturation level (%O₂) in the Napo streams as a function of grassland cover (**a,c,e,g**) and inundation extent (**b,d,f,h**) in the Napo streams, from Global Land Cover 2000¹¹⁴ and Global Inundation Extent from Multi-Satellites (GIEMS-D15)¹⁸ extracted from RiverATLAS⁶⁸. Symbols show the median and error bars the interquartile range, stations in the main-stem are shown by blue circles and in the tributaries by green squares, and solid lines show fits to the data (Supplementary Table 4).



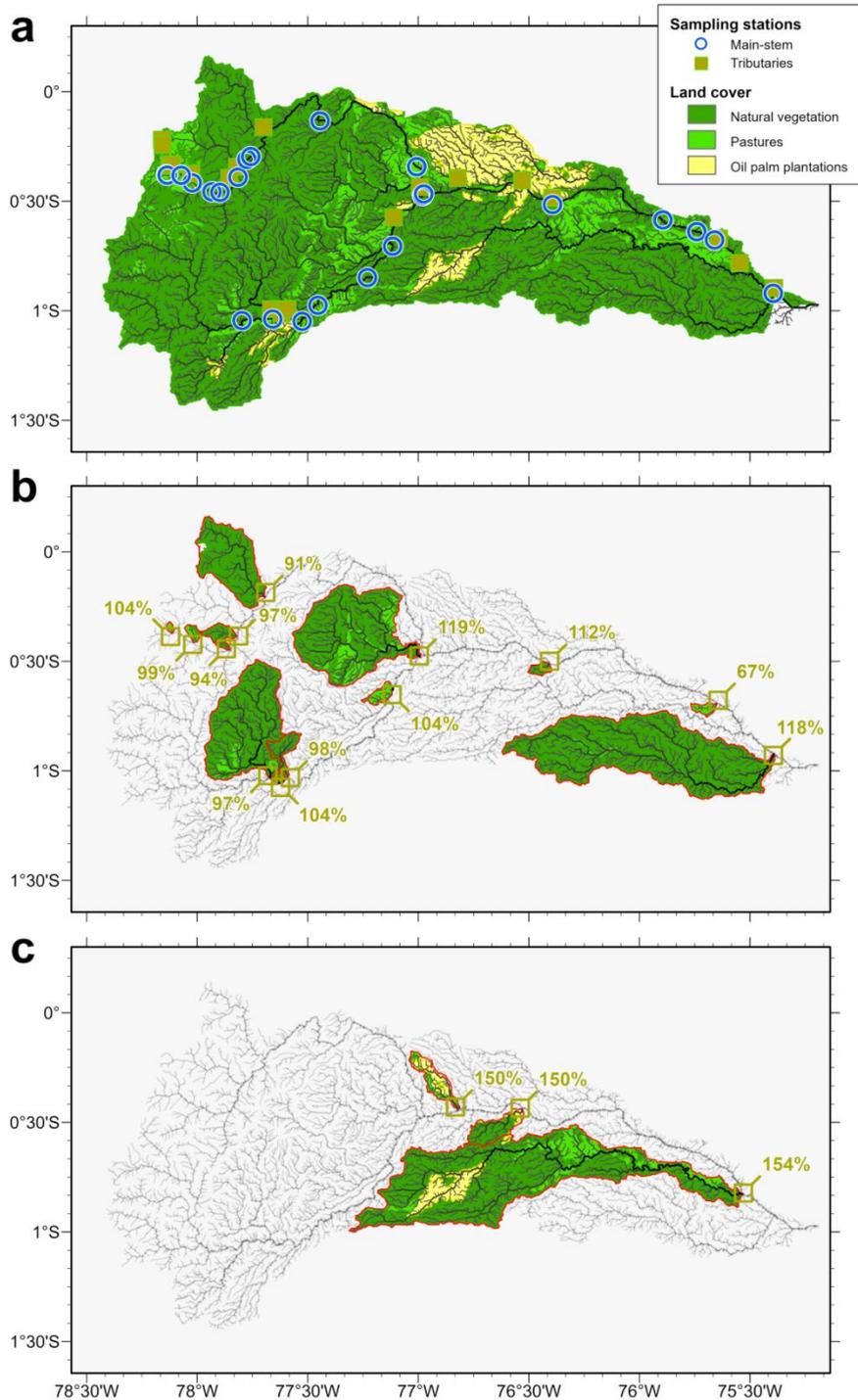
Supplementary Fig. 5 Elevation gradients of dissolved inorganic nitrogen in the Andean headwater and piedmont streams. Nitrate (NO_3^-), ammonia (NH_4^+) and dissolved inorganic nitrogen (DIN) concentration as a function of elevation in the Napo streams. Symbols show the median and error bars the interquartile range, stations in the main-stem are shown by blue circles and in the tributaries by green squares, and solid lines show fits to the data (Supplementary Table 4).



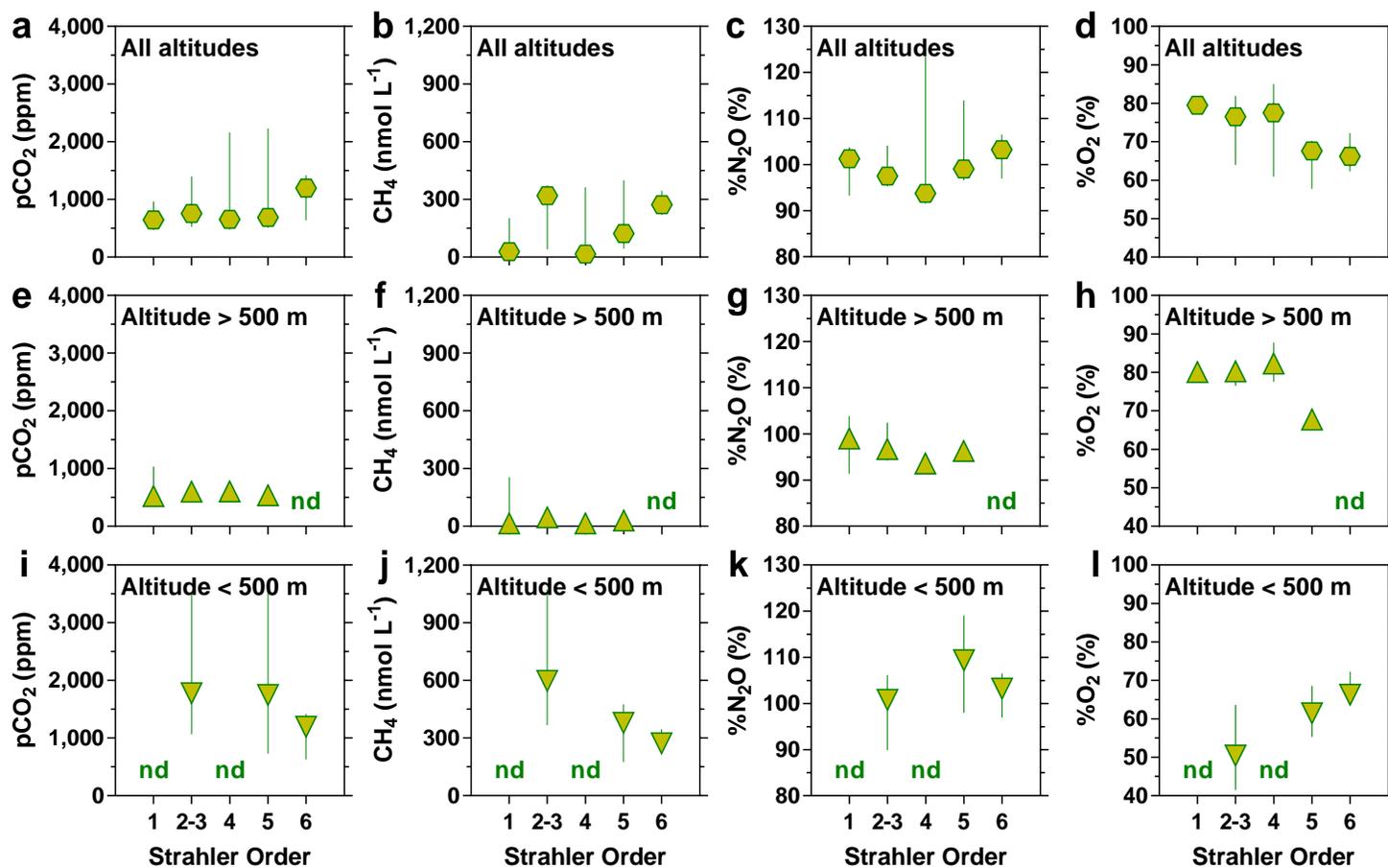
Supplementary Fig. 6 Aerial view of the Huirima stream showing meandering river course and presence of small lakes indicative of lateral inundation related to flat relief (low catchment slope). Landsat image was extracted from <https://earthexplorer.usgs.gov/> and is in the U.S. Public Domain.



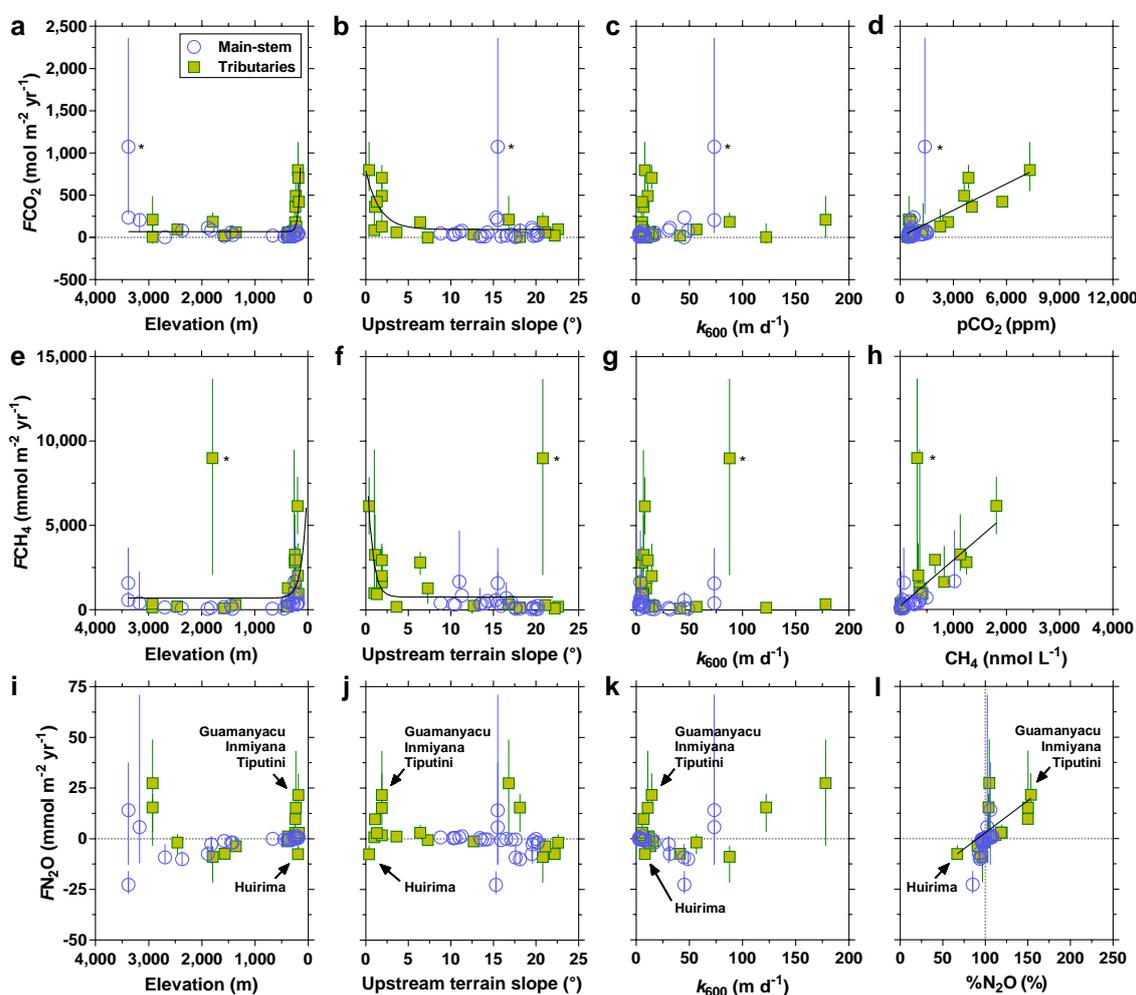
Supplementary Fig. 7 High N₂O levels are related to the presence of oil palm plantations in the Andean piedmont streams. Distribution of “natural” vegetation (merging forest and grassland) and agriculturally impacted land (pastures and oil palm plantations) in the Napo streams, for the whole catchment upstream of the most downstream station (a), and for individual catchments for N₂O saturation levels ≤ 119% (b) and ≥ 150% (c). Land covered by forest and grassland was merged into a single class (natural vegetation) by opposition to land cover strongly impacted by human activity (pastures and oil palm plantations). Stations in the main-stem are shown by blue circles and in the tributaries by green squares.



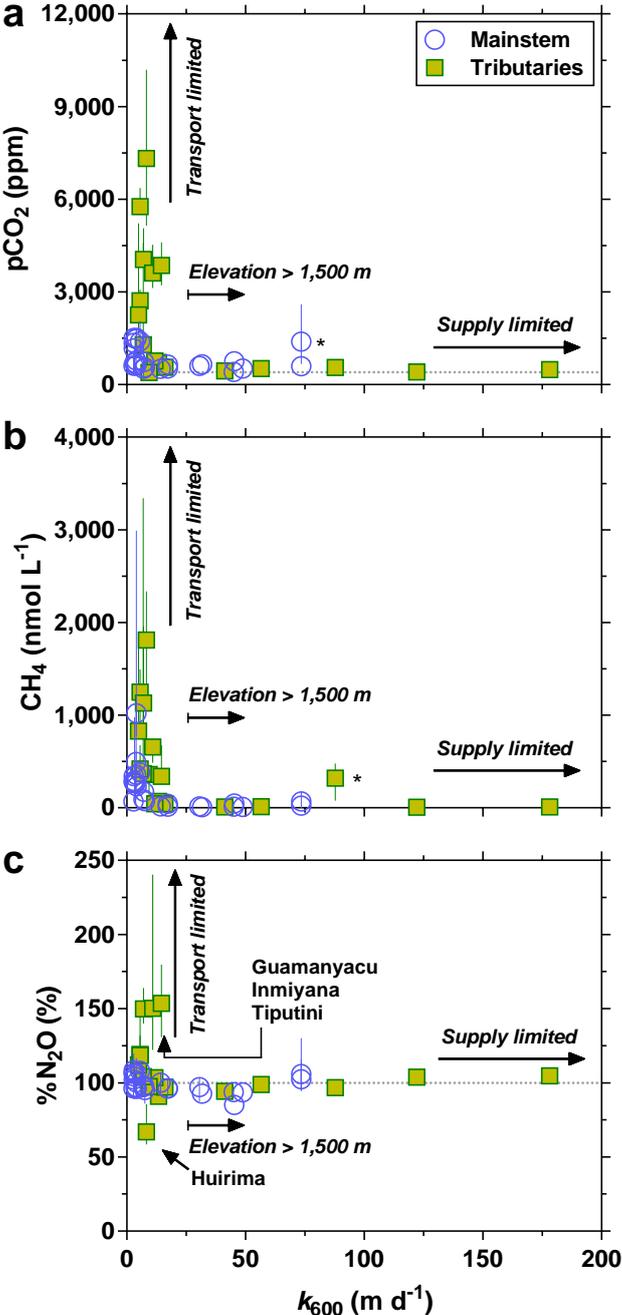
Supplementary Fig. 8 Low variations of pCO₂, CH₄ and %N₂O in the Andean headwater and piedmont streams as function of stream size. Variations of the partial pressure of CO₂ (pCO₂), CH₄ dissolved concentration, N₂O saturation level (%N₂O), and oxygen saturation level (%O₂) in the Napo streams as a function of Strahler order irrespective of elevation (**a,b,c,d**), for elevation > 500 m (**e,f,g,h**) and < 500 m (**i,j,k,l**). Due to low number of samples in low order streams, orders 2 and 3 were binned. Symbols show the median and error bars the interquartile range. nd = no data.



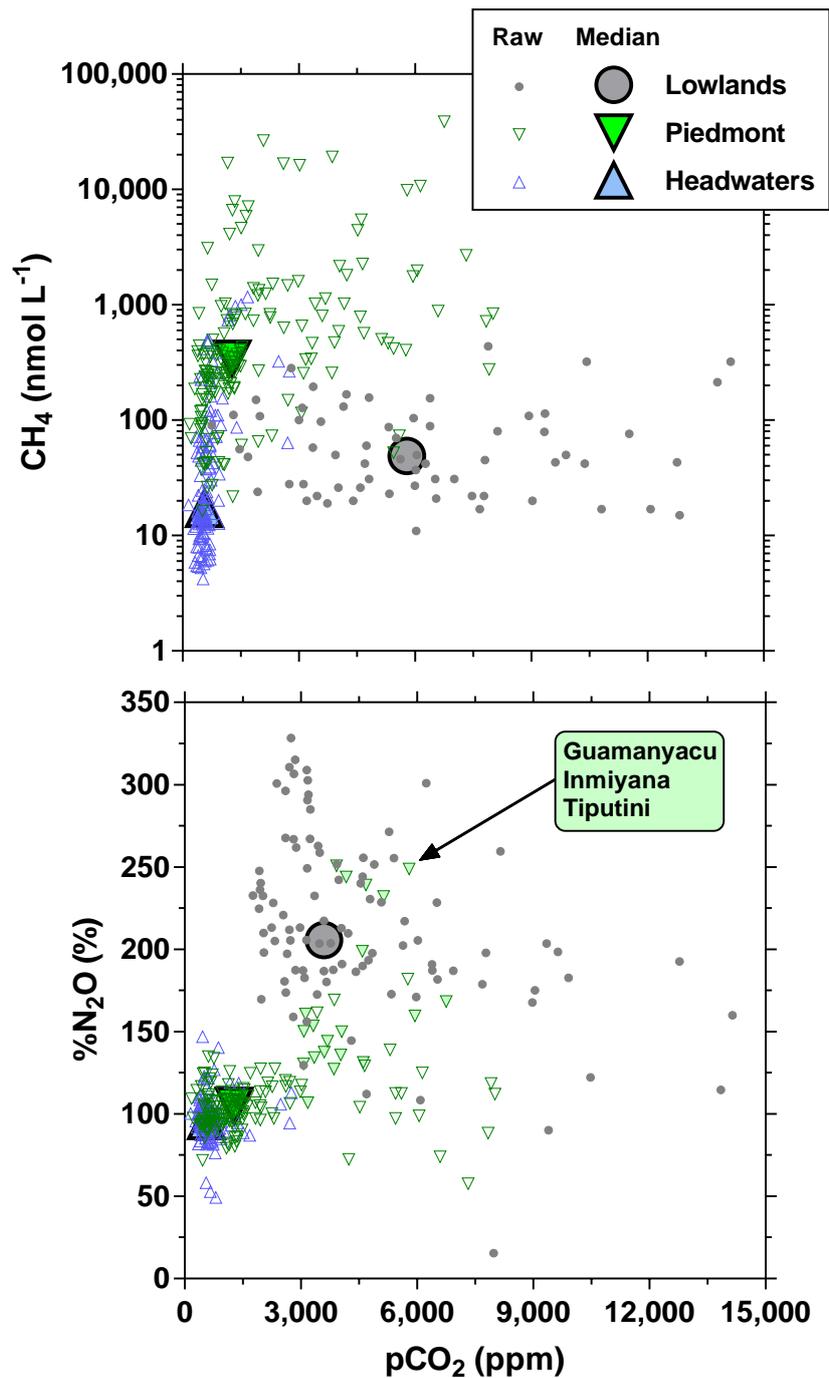
Supplementary Fig. 9 Strong elevation gradients of CO₂, CH₄ and N₂O emissions in the Andean headwater and piedmont streams. Air-water flux of CO₂ (F_{CO_2}) (a,b,c,d), of CH₄ (F_{CH_4}) (e,f,g,h) and of N₂O (F_{N_2O}) (i,j,k,l) as a function of elevation (a,e,i), upstream terrain slope (b,f,j), gas transfer velocity normalized to Schmidt number of 600 (k_{600}) (c,g,k), and respective dissolved gas content: partial pressure of CO₂ (pCO₂) (d), CH₄ dissolved concentration (h), N₂O saturation level (%N₂O) (l). Symbols show the median and error bars the interquartile range, stations in the main-stem are shown by blue circles and in the tributaries by green squares, and solid lines show fits to the data (Supplementary Table 4). Asterisk indicates streams with high CO₂ and CH₄ concentrations and high k_{600} values (refer to Fig. S10).



Supplementary Fig. 10 Transport-limitation or supply-limitation of the gaseous exchange with the atmosphere in the Andean headwater and piedmont streams. Partial pressure of CO₂ (pCO₂) (a), CH₄ dissolved concentration (b), and N₂O saturation level (%N₂O) (c) as a function of the gas transfer velocity normalized to Schmidt number of 600 (k_{600}). Symbols show the median and error bars the interquartile range, stations in the main-stem are shown by blue circles and in the tributaries by green squares, and solid lines show fits to the data (Supplementary Table 4). Asterisk indicates streams with high CO₂ and CH₄ concentrations and high k_{600} values leading to comparatively higher emissions (refer to Fig. S9).



Supplementary Fig. 11 Strong elevation gradients of CO₂, CH₄ and N₂O in streams and rivers across the whole Amazon basin. Variations of CH₄ dissolved concentration (a) and N₂O saturation level (%N₂O) (b) as a function of the partial pressure of CO₂ (pCO₂). Data in the lowland rivers and streams was compiled extracted from plots of Richey *et al.*³⁴ with Plot Digitizer (<http://plotdigitizer.sourceforge.net>). Small symbols show individual measurements, large symbols indicate the median, the blue triangles show the data in the mountainous headwater streams, green triangles show the data in piedmont streams, and the grey circles show the data in the lowland streams and rivers.



Supplementary Table 1 Comparison of air-water fluxes of CO₂ (*F*CO₂) and CH₄ (*F*CH₄) in the Amazon rivers and streams from this study and reported in literature^{5,16,27,30,31}. Only the diffusive component of *F*CH₄ is reported.

		<i>F</i> CO ₂ mol m ⁻² yr ⁻¹	<i>F</i> CH ₄ mmol m ⁻² yr ⁻¹
River channels < 150 m	This study	161±11	
	Reference ²⁷	156	
	Reference ⁵	157	
River channels ≥ 150 m	This study	91±6	
	Reference ²⁷	71	
	Reference ⁵	135	
Solimões/Amazon mainstem	This study		66±29
	Reference ³⁰		75
River channels ≥ 200 m	This study		199±55
	Reference ¹⁶		274±41
River channels (whole lowland basin)	This study		564±141
	Reference ³¹		370

Supplementary Table 2 Goodness of the linear regression of modelled partial pressure of CO₂ (pCO₂) based on three models versus observed pCO₂ from the Andean headwater and piedmont streams. The models were a linear regression (LR) as function of upstream slope, a multiple linear regression (MLR) as function of upstream slope and elevation, and a MLR as function of upstream slope and forest cover.

	Modelled pCO ₂ versus initial pCO ₂	r ²	Sy.x
Upstream slope LR	$y = 1.284 \pm (0.072) + 0.594 (\pm 0.023) * x$	0.59	0.202
Upstream slope + Elevation MLR	$y = 1.199 (\pm 0.071) + 0.620 (\pm 0.022) * x$	0.62	0.200
Upstream slope + Forest cover MLR	$y = 1.221 (\pm 0.071) + 0.613 (\pm 0.022) * x$	0.61	0.200

Supplementary Table 3 Comparison of stream surface area in the Amazon basin used in this study (extracted from RiverATLAS⁶⁸) and reported in literature^{5,16,27,30,31}. The surface area for large lowland rivers used by Sawakuchi *et al.*¹⁶ is two to three times higher than the range of values reported by Melack²⁷ for an equivalent river size class.

		Stream surface area km ²
River channels < 150 m	This study	16,304 (*)
	Reference ²⁷	31,000 (**)
	Reference ⁵	27,120 (***)
River channels ≥ 150 m	This study	21,668 (*)
	Reference ²⁷	29,500 (**) to 52,000 (****)
	Reference ⁵	25,500
Solimões/Amazon mainstem	This study	4,994 (*)
	Reference ³⁰	8,856
River channels ≥ 200 m	This study	19,828 (*)
	Reference ¹⁶	91,212 (*****)
River channels (whole lowland basin)	This study	40,375 (*)
	Reference ³¹	52,380 (*****)

* Reference⁶⁸

** Reference¹¹⁵

*** Reference¹⁰²

**** from Shuttle Radar Topography Mission

***** Reference¹¹⁶

***** Unspecified data source

Supplementary Table 4 Equations and statistics at 0.05 level of curve fits of data shown in Figures.

Figure	Function	Equation	Average Residual	r^2	p	n
2 a	pCO ₂ versus Elevation	$y = 7.730E+04 \cdot \text{EXP}(-1.768E-02 \cdot x) + 6.623E+02$	6.20E+02			44
2 b	pCO ₂ versus Upstream terrain slope	$y = 7.085E+03 \cdot \text{EXP}(-6.395E-01 \cdot x) + 8.108E+02$	5.14E+02			42
2 c	pCO ₂ versus Forest cover	$y = 2.773E-02 \cdot \text{EXP}(1.229E-01 \cdot x) + 9.977E+02$	5.56E+02			42
2 d	pCO ₂ versus Water temperature	$y = 6.775E-09 \cdot \text{EXP}(1.061E+00 \cdot x) + 3.882E+02$	7.14E+02			42
2 e	CH ₄ versus Elevation	$y = 1.695E+03 \cdot \text{EXP}(-5.725E-03 \cdot x) + 9.183E+01$	2.19E+02			44
2 f	CH ₄ versus Upstream terrain slope	$y = 1.202E+03 \cdot \text{EXP}(-6.150E-02 \cdot x) - 3.034E+02$	1.71E+02			42
2 g	CH ₄ versus Forest cover	$y = 1.804E+01 \cdot \text{EXP}(4.134E-02 \cdot x) - 2.591E+00$	1.83E+02			42
2 h	CH ₄ versus Water temperature	$y = 3.404E-02 \cdot \text{EXP}(3.844E-01 \cdot x) + 9.299E+01$	2.29E+02			42
2 i	%N ₂ O versus Elevation	$y = 7.940E+01 \cdot \text{EXP}(-9.046E-03 \cdot x) + 9.615E+01$	4.05E+00			40*
2 j	%N ₂ O versus Upstream terrain slope	$y = -0.8165 \cdot x + 112.3$		0.47	<0.0001	38*
2 k	%N ₂ O versus Forest cover	$y = 0.1619 \cdot x + 91.4$		0.20	0.006	38*
2 l	%N ₂ O versus Water temperature	$y = 9.648E-07 \cdot \text{EXP}(6.536E-01 \cdot x) + 9.610E+01$	3.62E+00			38*
2 m	%O ₂ versus log(Elevation)	$y = 18.953 \cdot x + 15.0$		0.40	<0.0001	44
2 n	%O ₂ versus Upstream terrain slope	$y = 1.3564 \cdot x + 50.1$		0.40	<0.0001	42
2 o	%O ₂ versus Forest cover	$y = -0.3749 \cdot x + 90.4$		0.31	0.0002	42
2 p	%O ₂ versus Water temperature	$y = -1.5737 \cdot x + 98.8$		0.40	<0.0001	44
3 a	pCO ₂ versus %O ₂	$y = 5.909E+04 \cdot \text{EXP}(-7.016E-02 \cdot x) + 4.755E+02$	4.97E+02			44
3 b	pCO ₂ versus CH ₄	$y = 0.2022 \cdot x + 39$		0.55	<0.0001	44
3 c	CH ₄ versus %O ₂	$y = 1.863E+04 \cdot \text{EXP}(-7.885E-02 \cdot x) + 1.335E+02$	4.97E+02			44
3 d	%N ₂ O versus pCO ₂	$y = 0.0053 \cdot x + 94.8$		0.46	<0.0001	40*
3 e	%N ₂ O versus %O ₂	$y = -0.2846 \cdot x + 120.2$		0.26	0.0009	40*
3 f	%N ₂ O versus DIN	$y = -0.9479 \cdot x + 106.5$		0.15	0.0126	40*
4 a	log(pCO ₂) versus log(Elevation)	$y = -0.308 \cdot x + 3.8443$		0.50	<0.0001	403
4 b	log(pCO ₂) versus log(Upstream terrain slope)	$y = -0.6519 \cdot x + 3.656$		0.57	<0.0001	403
4 c	log(CH ₄) versus log(Elevation)	$y = -0.1799 \cdot x^3 + 0.6348 \cdot x^2 - 0.1668 \cdot x + 1.7272$		0.40	<0.0001	471
4 d	log(CH ₄) versus Upstream terrain slope (for Elevation > 180 m)	$y = -0.0757 \cdot x + 3.0622$		0.42	<0.0001	297
4 d	log(CH ₄) versus Upstream terrain slope (for Elevation < 180 m)	$y = -0.1775 \cdot x + 2.5974$		0.21	<0.0001	174
4 e	log(CH ₄ :CO ₂) versus log(Elevation)	$y = -0.2342 \cdot x^3 + 0.9761 \cdot x^2 - 0.5717 \cdot x - 3.1345$		0.44		369
4 f	log(CH ₄ :CO ₂) versus Upstream terrain slope (for Elevation > 180 m)	$y = -0.0489 \cdot x - 1.8328$		0.22	<0.0001	305
4 f	log(CH ₄ :CO ₂) versus Upstream terrain slope (for Elevation < 180 m)	$y = -0.1094 \cdot x - 2.74$		0.08	0.0239	64
S2 a	Water temperature versus log(Elevation)	$y = -0.0001222 \cdot x + 1.406$		0.96	<0.0001	44
S2 b	k ₆₀₀ versus Elevation (for Main-stem)	$y = 0.01869 \cdot x - 2.266$		0.89	<0.0001	25
S2 b	k ₆₀₀ versus Elevation (for Tributaries)	$y = 0.0436 \cdot x - 5.528$		0.80	<0.0001	17
S3 a	Grassland cover versus Elevation (for Main-stem)	$y = 0.01994 \cdot x + 8.586$		0.93	<0.0001	25
S3 a	Grassland cover versus Elevation (for Tributaries)	$y = 0.01444 \cdot x - 3.572$		0.93	<0.0001	17
S3 b	Forest cover versus Elevation (for Main-stem)	$y = -0.01556 \cdot x + 68.6$		0.85	<0.0001	25
S3 b	Forest cover versus Elevation (for Tributaries)	$y = -0.01371 \cdot x + 86.13$		0.55	0.0025	17
S3 c	log(Inundation extent + 1) versus log(Elevation) (for Main-stem)	$y = -1.333 \cdot x + 4.702$		0.49	0.0001	25
S3 c	log(Inundation extent + 1) versus log(Elevation) (for Tributaries)	$y = -1.027 \cdot x + 3.604$		0.39	0.0078	17
S4 a	log(pCO ₂) versus log(Grassland cover + 1)	$y = -0.4003 \cdot x + 3.418$		0.53	<0.0001	39
S4 b	Inundation extent versus log(pCO ₂) (for Main-stem)	$y = 0.002844 \cdot x + 2.799$		0.35	0.0017	25
S4 b	Inundation extent versus log(pCO ₂) (for Tributaries)	$y = 0.01206 \cdot x + 2.858$		0.61	0.0002	17
S4 c	log(CH ₄) versus log(Grassland cover + 1)	$y = -0.8078 \cdot x + 2.95$		0.47	<0.0001	39
S4 d	log(CH ₄) versus Inundation extent (for Main-stem)	$y = 0.009493 \cdot x + 1.635$		0.34	0.0024	25
S4 d	log(CH ₄) versus Inundation extent (for Tributaries)	$y = 0.01461 \cdot x + 1.879$		0.27	0.0324	17
S4 e	log(%N ₂ O) versus log(Grassland cover + 1)	$y = -0.03509 \cdot x + 2.044$		0.35	0.0002	36*
S4 f	%N ₂ O versus Inundation extent (for Main-stem)	$y = 0.08749 \cdot x + 96.35$		0.34	0.0022	25*
S4 f	%N ₂ O versus Inundation extent (for Tributaries)	$y = 0.3674 \cdot x + 98.98$		0.64	0.001	13*
S4 g	log(%O ₂) versus log(Grassland cover + 1)	$y = 0.123 \cdot x + 1.685$		0.49	<0.0001	39
S4 h	log(%O ₂) versus log(Inundation extent+1) (for Main-stem)	$y = -0.02816 \cdot x + 1.875$		0.19	0.0309	25
S4 h	log(%O ₂) versus log(Inundation extent+1) (for Tributaries)	$y = -0.1262 \cdot x + 1.88$		0.46	0.0027	17
S5 b	NH ₄ ⁺ cover versus Elevation (for Main-stem)	$y = 2.104 \cdot x - 10.73$		0.57	<0.0001	25
S5 b	NH ₄ ⁺ cover versus Elevation (for Tributaries)	$y = 1.58 \cdot x - 8.237$		0.71	<0.0001	17
S5 c	DIN cover versus Elevation (for Main-stem)	$y = 1.989 \cdot x - 5.851$		0.45	0.0004	25
S5 c	DIN cover versus Elevation (for Tributaries)	$y = 1.593 \cdot x - 4.679$		0.62	<0.0001	17
S9 a	FCO ₂ +2 versus Elevation	$y = 3.858E+04 \cdot \text{EXP}(-2.674E-02 \cdot x) + 7.031E+01$	1.05E+02			42
S9 b	FCO ₂ +2 versus Upstream terrain slope	$y = 6.936E+02 \cdot \text{EXP}(-6.181E-01 \cdot x) + 9.523E+01$	1.10E+02			42
S9 d	FCO ₂ versus pCO ₂	$y = 0.1045 \cdot x + 6.451$		0.45	<0.0001	42
S9 e	FCH ₄ versus Elevation	$y = 7.324E+03 \cdot \text{EXP}(-1.036E-02 \cdot x) + 6.882E+02$	9.56E+02			42
S9 f	FCH ₄ versus Upstream terrain slope	$y = 9.751E+03 \cdot \text{EXP}(-1.635E+00 \cdot x) + 7.622E+02$	8.02E+02			42
S9 h	FCH ₄ versus CH ₄	$y = 2.711 \cdot x + 217$		0.38	<0.0001	42
S9 i	FN ₂ O versus N ₂ O	$y = 0.316 \cdot x - 28.72$		0.13	0.0206	42

* Excluding Guamanyacu, Imiyana, Tiputini, and Huirima Rivers

References

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