

Supporting material

Summary of analytical methods

Table S1 provides a summary of all analytical methods used in the study.

Table S1. Summary and overview of the presented analyses carried out on sediment samples and water samples, year of collection and analysis, type of sediments/water, number of samples, the laboratories where the analyses were carried out and reference to analyses methodology.

Type of analysis	Samples collected ^a	Samples analysed	Type of sed. / water ^b	No of sampl.	Laboratory: methodology
SEDIMENT					
Exchangeable NH ₄ ⁺	2007	2008	H, P	21	INST: ^c
N-mineralization potential	2007	2007	H, P	4(×2)	CETASD: Johansson et al. (1999)
Exchangeable NH ₄ ⁺	2003, 2007	2007	H, P	19	CETASD: Johansson et al. (1999) (on un-incubated samples)
Exchangeable NH ₄ ⁺	2003, 2006	2006	H, P, S	6	KTH: Bremner and Keeney (1966)
δ ¹⁵ N of exchangeable NH ₄ ⁺	2007	2008	H, P	21	INST: Kelley et al. (1991), Stark and Hart (1996), and Khan et al. (1998) with minor modification ^d
δ ¹⁵ N of total N, δ ¹³ C of total C	2003 ^a	2006	H, P	2	SLU: Ohlsson and Wallmark (1999)
LOI	2007	2008	H, P	20	GU: Heiri et al. (2001) and Bengtsson and Enell (1986)
WATER					
Metals; NH ₄ ⁺ ; PO ₄ ³⁻ ; As(III); As(V); trace el.	2006, 2007	2006, 2007	H, P, S	42	Eawag: see Berg et al. (2008) and Norrman et al. (2008)
Major anions, Alkalinity, DOC	2006, 2007	2006, 2007	H, P, S	42	Eawag: see Berg et al. (2008) and Norrman et al. (2008)
NH ₄ ⁺	2006, 2007	2006, 2007	H, P, S, Sewage	12	INST: ASTM standard method D6919-03 (2003)
δ ¹⁵ N in NH ₄ ⁺	2006, 2007	2006, 2007	H, P, S, Sewage	22	INST: Kelley et al. (1991), Stark and Hart (1996), and Khan et al. (1998) with a minor modification ^d .
δ ¹⁵ N and δ ¹⁸ O in NO ₃	2006, 2007	2006, 2007	H, S	4	INST: Chang et al. (1999), Silva et al. (2000), Kendall and Grim (1990) with minor modification ^e .
Bacteriological content	2007	2007	H, P	9	INST: ISO 9308-1990 standard

a) Samples from the drillings in 2003 were stored in open air until 2006.

b) H – Holocene sediments/aquifer, P – Pleistocene sediments/aquifer, S – Surface sediments/surface water (sewage settling ponds and Red River) and/or shallow groundwater.

c) Upon arrival, sediment samples were stored in a freezer at –24°C. For analysis, the samples were first dried at 70°C overnight and grounded to homogenize the content. The samples were sieved (1 mm mesh) and approximately 10 g of the sieved sediment was mixed with 100 ml of 2 M KCl. The mixture was shaken on a horizontal shaker for 1 hour (Khan et al., 2000). The suspension was filtered using a glass fiber filter (Whatman) and the retained sediment was washed three times with 30 ml of 2 M KCl. The solution was analyzed for exchangeable ammonium by spectrophotometry using the Nessler reagent and an UVmini-1240 (Shimadzu, Japan) on the wavelength of 490 nm (Bremner & Keeney, 1965).

- d) The filters with the trapping reagent were sealed between a Teflon membrane by a hand press. Filtered (0.45 μm mesh) water samples of 20-100 ml (depending on ammonium content) were placed in wide mouth Mason jars with plastic screw caps (see Khan et al., 1998, for a picture of jar). The traps were dropped in, and allowed it to float over the surface of the water samples, instead of hanging the trap over the samples. 25 ml KOH 5M was carefully pipetted to the sample from the jar's bottom. After all the alkaline was gone from the pipette, the jar's cap was immediately screwed tightly and sample content in the jar was gently swirled for 20-30 s. The samples were allowed to incubate for six days with occasional swirling to facilitate the ammonia to diffuse through the Teflon membrane to the trap. Upon completion of the diffusion period, the trap was removed and placed on a rack inside a desiccator containing CaO to dry. When the isotopic analysis to start, individual disc trap was wrapped in a tin capsule for further combustion in a quartz tube filled with quartz chips mixed with Cu and CuO powder to convert ammonium in the salt $[\text{K}(\text{NH}_4)\text{SO}_4]$ into nitrogen gas. Nitrogen in atmospheric air is used as standard to calculate $\delta^{15}\text{N}$. The precision of the $\delta^{15}\text{N}$ analysis is 0.2‰.
- e) The modification was that the AgNO_3 was wrapped in tin capsules and then dropped by the autosampler in a combustion tube made from quartz and filled with quartz chips mixed with Cu, CuO and Ag powder to form nitrogen gas. The combustion tube was installed in an oven inside the Elemental Analyzer. In the analysis of ^{18}O , the nitrate combustion was carried out in a glassy carbon tube filled with glassy carbon chips and CuO powder to form CO_2 . Any contaminant associated with the gases was purified by a gas chromatographic column connected just on the exit from the combustion tubes. The water standard supplied by the IAEA (Coplen, 1996) is used to calculate $\delta^{18}\text{O}$. The precision of oxygen-18 analysis is 0.2‰.

Results

Table S2 summarises the results from the water analyses in the study.

Table S2. Concentrations of selected species in water collected in Nam Du and Dan Phuong during the dry season in 2006 and 2007.

	Place	Date	Depth	T	pH	Eh	Na	Ba	Ni	Cl	K	NO ₃ -N	NH ₄ -N	PO ₄	DOC	δ ¹⁵ N NH ₄ -N	As(tot)	As(III)
	ID	m/d/y	m	°C		mV	mg/L	µg/L	µg/L	mg/L	mg/L	mg/L ^{b)}	mg/L	mg/L ^{c)}	mg/L	‰ ^{d)}	µg/L	µg/L
Holocene	P1B	2/20/06	23	26.5	6.68	-132	32.0	399	52	5.8	7.4	<0.25	40.3	0.19	10.5	21.2	264	254
	P2B	3/10/07	26	27.0	7.35	-128	65.5	218	3.2	58.7	19.8	3.4	20.7	1.42	8.5		18	12
	P3B	2/20/06	22	24.5	6.29	48	27.3	287	3.0	41.9	1.8	<0.25	2.1	0.71	9.0	11.1	39	34
	P3B	3/10/07	22	26.7	6.47	-137	48.1	313	1.4	69.5	7.8	<0.25	31.8	3.18	11.3		23	27
	P86B	2/20/06	19	24.4	6.90	-85	11.2	175	50	10.1	1.4	<0.25	2.6	<0.2	2.4		62	56
	P86B	3/11/07	19	26.0	7.15	-111	9.9	433	12	11.0	1.6	2.2	2.4	<0.2	1.4		70	63
	DHA14	4/20/07	14	25.9	6.93	-201	33.6	662	1.1	14.7	4.7	<0.25	13.8	0.87	2.7	17.9	483	479
	DHA18	4/20/07	18	26.1	7.00	-180	19.3	493	2.1	20.5	5.8	<0.25	22.1	0.93	3.0	21.5	457	444
	DHA22	4/20/07	22	25.9	6.85	-184	14.7	517	0.32	25.2	3.6	<0.25	9.4	1.29	1.8	15.9	355	336
	DHA30	4/20/07	30	26.3	6.37	-153	15.9	552	0.29	4.8	3.3	<0.25	36.2	2.43	4.5	20.6	170	173
	DHB14	4/20/07	14	26.5	7.08		45.2	542	3.4	37.4	11.6	<0.25	20.7	0.40	10.6	19.3	150	147
	DHB18	4/20/07	18	26.2	6.52	-131	29.3	495	3.0	10.2	3.6	<0.25	11.9	0.49	3.0	16.5	265	230
	DHB22	4/20/07	22	25.9	6.83	-168	16.2	379	0.40	10.1	3.9	<0.25	6.9	0.88	2.1	12.5	325	306
	DHB26	4/20/07	26	26.1	6.40	-161	23.7	577	0.74	8.3	3.8	<0.25	30.5	2.26	8.7	20.5	218	221
Pleistocene	DP4 ^{a)}	4/-/07	4										0.3			na		
	DP5 ^{a)}	4/-/07	5										3.3			5.4		
	DP12 ^{a)}	4/-/07	12										0.3			na		
	DP13 ^{a)}	4/-/07	13										3.9			4.6		
	P1A	2/20/06	57	27.4	7.11	-159	23.5	228	0.76	10.3	4.6	<0.25	12.7	0.95	4.0	17.3	257	258
	P1A	3/10/07	57	26.2	6.65	-111	23.1	205	1.0	11.3	4.3	<0.25	11.8	0.94	2.6		226	212
	P2A	3/10/07	47	26.9	8.28	-81	20.5	202	2.3	11.4	4.9	<0.25	14.6	0.86	2.4		134	129
	P3A	2/20/06	47	27.4	6.29	43	37.7	417	3.9	30.2	4.1	<0.25	24.0	1.05	12.2	19.5	152	148
	P3A	3/10/07	47	27.4	6.42	-133	37.1	370	3.5	46.2	3.8	<0.25	26.3	1.04	13.1		157	137
	P86A	2/19/06	57	26.2	6.95	-125	23.6	218	0.74	16.2	3.9	<0.25	16.4	0.71	2.9	18.2	312	282
	P86A	3/10/07	57	26.5	6.88	-114	28.2	293	0.52	18.7	3.9	<0.25	12.7	0.79	2.0		277	260
	DHA52	4/20/07	52	26.5	6.76	-181	13.6	233	1.0	5.3	3.9	<0.25	11.8	0.67	2.1	17.8	73	74
	DHB52	4/20/07	52	26.6	6.63	-140	29.6	248	2.4	18.5	5.8	<0.25	16.4	0.73	3.6	15.3	41	41
	PX	2/22/06	70	27.2	6.31	-42	17.3	205	0.39	5.1	4.3	<0.25	3.2	0.24	2.1		27	27
ND3	2/14/06	60	26.5	6.65	-138	6.9	231	1.5	2.2	3.2	<0.25	9.3	0.88	2.6	16.3	83	63	
ND9	2/14/06	60	27.0	6.35	-94	17.5	292	1.5	8.0	4.4	<0.25	8.6	0.46	2.7	12.7	83	77	
ND9	3/6/07	60	26.4	6.47	-80	17.4	222	1.0	6.6	4.2	<0.25	7.6	0.52	1.7		76	74	
ND12-	2/19/06	65	25.9	7.10	-124	4.5	89	0.46	1.5	2.0	<0.25	1.8	<0.2	2.0	13.7	44	39	

	4(A,C)																	
	ND13	3/6/07	60	25.5	6.86	-13	17.6	103	0.87	4.3	3.4	<0.25	5.6	<0.2	1.0	13.7	81	99
	DP65 ^{a)}	4/-/07	65										3.0			6.2		
Ponds	Pond 1	2/14/06	0	25.1	8.21	109	28.8	124	1.9	27.6	20.2	<0.25	1.6	<0.2	9.4	10.3	4.9	
	Pond 2	2/15/06	0	23.7	7.40	131	14.4	81	1.2	14.7	7.3	<0.25	9.0	<0.2	5.2	16.1	2.6	
	Pond 3	2/15/06	0	24.8	7.54	141	17.8	99	2.5	11.6	6.8	0.36	2.4	<0.2	6.1		1.9	
River water	RR2	2/14/06	0	23.8	8.00	160	4.1	106	0.84	2.7	1.2	0.31	0.1	<0.2	2.0	5.3	2.8	
	RR2	3/11/07	0	19.1	8.35	-39	4.2	119	0.45	2.5	1.4	<0.25	0.1	<0.2	1.3		3.6	1.9
	RR3	3/11/07	0	19.4	7.79	-64	4.9	20	0.36	2.5	1.6	0.3	0.13	<0.2	1.0		3.4	0.7
	RR4	3/8/07	0	19.2	8.19	125	5.4	118	0.54	2.8	1.7	0.4	0.1	<0.2	1.2		4.0	1.3
Shallow groundwater	RB1	2/15/06	0.3	23.9	7.08	180	4.1	58	0.71	2.6	2.1	<0.25	0.45	<0.2	1.7	6.4	2.6	0.9
	RB2	2/15/06	0.3	24.6	7.30		4.3	104	0.46	2.5	2.9	<0.25	0.1	<0.2	1.9		0.4	0.2
	RB2	3/11/07	0.3	18.8	7.05	-18	7.2	356	1.6	3.1	3.2	1.1	0.7	<0.2	2.3		22	24
	RB3	3/1/06	0.3	16.7	8.69	5	4.4	31	0.41	2.7	1.5	0.61	0.4	<0.2	3.3		2.6	1.8
	RB3	3/11/07	0.5	18.2	7.05	-8	10.5	516	5.5	4.1	7.2	1.9	12.1	<0.2	21.7		134	111
	RB4	3/8/07	0.5	18.3	7.18	-87	7.4	446	2.6	3.7	5.3	4.8	5.1	<0.2	6.2		173	158
Sewage water	SW-A	3/8/07	0										3.1			15.4		
	SW-B	3/8/07	0										0.13			1.6		

a) DP stands for Dan Phuong. All samples from Dan Phuong had traces of NO₃.

b) <0.25 denotes below detection limit for NO₃

c) <0.2 denotes below detection limit for PO₄

c) accuracy ±2‰

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