

ລະດັບຄວາມເຂັ້ມຂຸ້ນຂອງທາດເຫຼັກ ແລະ ມັງກາແນເຊີ ທີ່ບັນຈຸໃນ ຜັກນ້ຳ ປູກຢູ່ອ່າງໂຕ່ງ ຫ້ວຍປ່ານໍ້ ແຂວງຫຼວງພະບາງ

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ບົດຄັດຫຍໍ້

ການປາກົດຕົວຂອງໂລຫະໜັກຢູ່ໃນຜັກບາງຊະນິດເຊັ່ນ: ຜັກນ້ຳ ອາດສົ່ງຜົນສະທ້ອນທາງລົບ ຕໍ່ສຸຂະພາບ. ຜັກນ້ຳ ຊຶ່ງມັກເກີດຢູ່ຫ້ວຍນ້ຳໄຫຼ ແລະ ມັກພູມອາກາດຊຸ່ມຊື່ນ ໃນເຂດພູດອຍ. ບົດນີ້ ໄດ້ສຶກສາການສະສົມຂອງທາດເຫຼັກ ແລະ ມັງກາແນເຊີໃນຜັກນ້ຳ ທີ່ປູກຢູ່ບໍລິເວນສາຍຫ້ວຍທີ່ມີສະພາບພື້ນທີ່ແຕກຕ່າງກັນ. 2 ຈຸດທົດລອງປູກຜັກນ້ຳ ເຂດທີ່ມີນ້ຳໄຫຼຢອດຫ້ວຍ (ມີອີກຊີຫຼາຍ) ແລະ ເຂດເບືອມນ້ຳ (ມີອີກຊີໜ້ອຍ) ໄດ້ສົມທຽບເພື່ອສຶກສາຄວາມເຂັ້ມຂຸ້ນຂອງທາດເຫຼັກ ແລະ ມັງກາແນເຊີທີ່ສາມາດລະລາຍ ແລະ ແລກປ່ຽນໄດ້. ຜົນການສຶກສາຊີ້ໃຫ້ເຫັນວ່າ ປັດໄຈສິ່ງແວດລ້ອມ ເປັນຕົວກຳນົດລະດັບຂອງໂລຫະໜັກໃນຜັກ. ຖ້າດິນບັນຈຸທາດໂລຫະໃນປະລິມານຫຼາຍ ຜັກນ້ຳກໍ່ຈະດູດຊັບເອົາທາດເຫຼັກ ແລະ ມັງກາແນເຊີ ຫຼາຍເຊັ່ນດຽວກັນ. ລະດັບຄວາມເຂັ້ມຂຸ້ນຂອງທາດມັງກາແນເຊີ ບັນຈຸໃນຜັກນ້ຳຈະເພີ່ມຂຶ້ນ 7.5 ເທົ່າ ແລະ ທາດເຫຼັກ 2.2 ເທົ່າ ໃນເຂດເບືອມນ້ຳ (ມີອີກຊີໜ້ອຍ) ເມື່ອສົມທຽບກັບເຂດທີ່ມີນ້ຳໄຫຼຢອດຫ້ວຍ (ມີອີກຊີຫຼາຍ). ສະຫຼຸບວ່າ ຄວາມເຂັ້ມຂຸ້ນຂອງທາດເຫຼັກ ແລະ ມັງກາແນເຊີໃນດິນ ແມ່ນກົງກັນກັບຄວາມເຂັ້ມຂຸ້ນຂອງທາດເຫຼັກ ແລະ ມັງກາແນເຊີ ທີ່ບັນຈຸໃນຜັກ.

Iron and manganese concentration levels in watercress cultivated within the main stream of the Houay Pano catchment, Northern Lao PDR

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Abstract

The bio-availability of metals to currently eaten aquatic herbs such as watercress is of important interest because of its potential impact on human health. Watercress grows in clear running water and is suited to the moist climates of mountainous tropical regions. In this study, the concentrations of Fe and Mn in watercress, stream bottom sediments and ambient stream water were measured in order to evaluate the impact of local environmental conditions on plant Fe- and Mn- accumulation levels. Two sites in the Houay Pano catchment in northern Laos (Luang Prabang province) where watercress is cultivated directly in the stream waters were selected for their contrasting environmental conditions (oxic vs. dysoxic to suboxic oxygen levels). Total, dissolved, exchangeable and potentially exchangeable Fe- and Mn- concentrations were measured. The results indicate that local environmental factors are determinant factors in the availability of these ionic species. Both the total metal content in the sediments and the metal ion speciation status (availability of dissolved species) determine the level of Fe and Mn uptake by watercress. The concentration levels in watercress increased by a factor of 7.5 for Mn and 2.2 for Fe in the dysoxic to suboxic site (swampy area) compared to the oxic site (upstream running water). The exchangeable and potentially exchangeable Fe- and Mn- concentrations in bottom sediments and the dissolved Fe- and Mn- contents of ambient water at both sites were consistent with the accumulation levels measured in the watercress.

The bioaccumulation of these metals should not pose a direct threat in itself, because these elements are not actually very toxic, but rather it is indicative of the local physico-chemical conditions that could be potentially favoring the mobility and accumulation of toxic metals such as the so-called atmophile elements (e.g. Cu, Cd, Zn, As). These elements are the subject of an ongoing study. Because watercress appears to easily accumulate metals it could be used to clean contaminated water by soaking up the toxic elements.

Key words: *Aquatic herbs; Metal bioaccumulation; Mountainous environment; Bioremediation, Lao P.D.R*

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Introduction

Potentially toxic metals may accumulate in soils and sediments along the banks of river systems. Metals are either derived directly from man made waste accumulation (i.e. industrial waste, sewage sludge disposal, fertilizer application on crop fields) or, indirectly removed from naturally occurring metals, located within mineral structures or sorbed onto mineral surfaces. Their natural concentrations in soils define part of the so-called "soil geochemical background", inherited from the composition of the rocks of the geological basement. Metals may contaminate surface and ground waters connected to the river system (Naiman et al., 2005). Health authorities recommend very low metal concentrations in drinking water, for example in France these values are $5 \mu\text{g l}^{-1}$, $10 \mu\text{g l}^{-1}$, $50 \mu\text{g l}^{-1}$ and $200 \mu\text{g l}^{-1}$ for Cd, Pb, Mn and Fe, respectively (Décret 2001-1220, December 12, 2001). Metal bio-availability generally refers to the ability of a given element to be transferred from soil (or sediment) to water. Plants take up most of their trace nutrients from water and can therefore potentially accumulate metals if available. Uptake of Fe and Mn by plants depends mainly on soluble pools and the ability of plant

roots to reduce these metals to their mobile forms (i.e. Fe^{3+} to Fe^{2+} and Mn^{4+} or Mn^{3+} to Mn^{2+}). Although these processes are controlled by microbiological activity they may be monitored by environmental parameters: temperature, pH, Eh (redox potential); dissolved oxygen concentration and turbidity, which affect the behavior of metals in natural waters (Stumm and Morgan, 1996). From a purely geochemical point of view, the extent of metal adsorption by plants is controlled by: (1) the total metal content and, (2) the metal ion speciation status in the soil or sediment (Kabata-Pendias, 1993; Alloway, 1995). Both parameters are influenced by the "free metal ion" concentration in the pore water (i.e. the Fe^{2+} concentration with respect to the total Fe concentration), which is linked to the presence of soluble organic and inorganic complexes (Benedetti et al., 1996). Both adsorption onto Fe-Mn-oxides and hydroxides surfaces and complex formation with organic matter reduce the amount of "free metal ions" in the water and thus, the extent of metal uptake by aquatic plants. Several studies have shown that the reactivity of trace metals is strongly linked to the presence of oxides and hydroxides in soil and sediments (e.g. Kabata-Pendias and Pendias, 2001; Dumat et al., 2001).

Antagonist interactions between metals also occur, i.e. excess amounts of Mn in plants, reduces absorption and translocation of Fe, resulting in a decrease of chlorophyll and photosynthesis.

The issue of metal bio-availability to aquatic herbs, in particular watercress (*Nasturtium officinale*), is of important interest because this cultivated plant is currently eaten raw as salad or cooked as a vegetable. Metal concentrations in commonly consumed watercress are usually very low, ca. 0.009 - 0.3 g kg⁻¹ and ca. 0.002 - 0.03 g kg⁻¹ for Fe and Mn, respectively (Cumbus et al., 1980; Mohamed et al., 2003; Kawashima and Soares, 2003). However, much higher amounts were reported, up to 7.6 ± 0.7 g kg⁻¹ for Fe and to 08 ± 0.2 g kg⁻¹ for Mn, for iron-contaminated sites in China (Wong, 1985). Watercress grows in clear running waters and is suited to temperate environments or the relatively cool moist climates of mountainous tropical regions (Herklots, 1972). In the province of Luang Prabang (northern Laos), watercress is usually grown from cuttings and planted in waterlogged areas. On the Houay Pano catchment near Luang Prabang, local cultivation is set up directly in the main stream. The aim of this study was to measure

the total Fe- and Mn- accumulations in watercress grown in this watershed and to compare these concentration levels with those determined for bottom sediment and ambient water. These determinations provided a first-order estimate of potential metal accumulations in sediments and plants in relation to the local environmental conditions.

Materials and methods

The biophysical and socio-economic characteristics of the study area are described in detail by Valentin et al. (this issue). The geological basement of the catchment is composed of Permian to Upper Carboniferous sedimentary to low grade metamorphic rocks (schists, mudstones and fine-grained sandstones) overlaid by limestone cliffs. Soils are cultivated on steep slopes (average slope: 60 %) by slash-and-burn with no fertilizer input. The soils of the area are dominated by entisols (18.5 %; clay soils with medium fertility, pH = 6.4), ultisols (33.1 %; clay soils with medium fertility, pH = 5.5), and alfisols (48.5 %; heavy clay soils with medium fertility, pH = 6.2). The stream in which watercress is grown is a third order tributary of the Mekong, located 10 km south of Luang Prabang. The permanent flow is fed by

groundwater (i.e. $1.6 - 5.2 \text{ l s}^{-1}$; Ribolzi et al, 2005) during the dry season. During the rainy season, the water level is controlled by the amount of rain and the soil saturation status.

Cultivated watercress, bottom sediments and water samples were collected in March 2007 during the dry season from two different sites, located in the upper (site A) and central part (site B) of the catchment (Figure 1). Both sites are included in a monitoring survey of groundwater inflow and outflow in the main stream of the Houay Pano catchment (Ribolzi et al., 2005). The environmental parameters measured the day of sample collection (3/7/2007, 11 am - 2 pm, Table 1) indicate that site A has "oxic conditions" ($[\text{O}_2] > 2.9 \text{ mg l}^{-1}$, Tyson and Pearson, 1991). However, site B is located in a swampy zone where "dysoxic" to "suboxic" conditions prevail ($2.9 < [\text{O}_2] < 0.0 \text{ mg l}^{-1}$; Tyson and Pearson, 1991). For site B, it is of note that watercress only grows in areas where oxygen levels are high (samples B1 - B6, Table 2).

Two different techniques were applied for water sampling: **(1)** a conventional technique with water collection in plastic bottles and filtering through a $0.2 \mu\text{m}$ acetate filter, in order to separate

suspended solid material from dissolved (and colloid) material and; **(2)** in-situ selective metal extractions, based on a DGT procedure (Diffusive Gel Transfer, Zhang et al., 1995). The DGT device uses a specific layer of Chelex resin, impregnated in a hydrogel to accumulate the metals. Ions must diffuse through the filter and the diffusive layer of hydrogel to reach the Chelex resin. The DGT devices were immersed in the stream at sites A and B, very close to watercress cuttings and were recovered after 3 days. This procedure accumulates "free metal ions" on the resin and, thus, very low concentration levels may be determined in natural waters, in particular when these levels are below the detection limits of currently used chemical analyzers. Fe and Mn concentrations were calculated using the procedure described in Zhang et al. (1995) with temperature corrections required for the application of diffusion gradients. Total Fe- and Mn- concentrations were determined by Atomic Absorption Spectroscopy (Unicam 989 QZ and Unicam AA series, detection limit: 0.5 ppb).

Watercress samples were dried, weighed and grounded. Aliquots (200 mg) were dissolved in 2 ml of 0.43M HNO_3 and 1 ml of 30 % H_2O_2 for 24

h at 100°C. After dissolution, solid vegetation residues represented less than 10 % of the initial sample weight. The solutions were centrifuged at high speed to remove any solid material and filtered through a 0.2 µm acetate filter. Sediment samples were finely grounded. Selective extractions were carried out on two replicate sample aliquots (2 g) using procedures described in Dumat et al. (2001). Exchangeable (= soluble in water) Fe and Mn were extracted with 0.01M CaCl₂ during 24 hours at 20°C. Potentially exchangeable metals (= bound to oxides and/or hydroxides) were extracted from two replicate sample aliquots (2 g) with 0.43M HNO₃ and 6M HCl for 2 hours at 20°C. The solution recovered for both extraction procedures were centrifuged and filtered as described for the vegetation samples. The total organic carbon (TOC) and total nitrogen (TN) concentration of sediments were determined using a Carlo-Erba elemental analyzer (Girardin and Mariotti, 1991). All measurements (Tables 2 - 4) were carried out in the laboratories of UMR Bioemco (Université Pierre & Marie Curie) in Paris.

Discussion and interpretation

Fe and Mn concentrations in watercress and bottom sediments

In general total Fe- and Mn-accumulations in plants show remarkable variations depending on the plant species, soil type, stage of growth, as well as ecosystem (Kabata-Pendias and Pendias, 2001). The minimum Mn level for most plants is 0.015 - 0.025 g kg⁻¹ but may increase above 1.0 g kg⁻¹ for some species. A large range is also observed for Fe in plants, ranging from 0.02 g kg⁻¹ up to 3.5 g kg⁻¹. Because watercress grows in waterlogged or aquatic systems, Mn and Fe are more easily available and plant concentrations should fall in the upper range. It was observed that the total Fe and Mn contents in watercress were higher for site B (swampy area) than for site A (upstream). Fe and Mn concentrations ranged from 14.1 - 46.5 and 21.1 - 26.6 g kg⁻¹ and 4.4 - 19.6 g.kg⁻¹ and 1.0 - 10.0 g.kg⁻¹, for sites B and A, respectively (Table 3). A simple explanation for this difference is the contrasting redox status of each environment. However, significant variations linked to the environmental parameters are also observed locally (Table 2). The dissolved oxygen content

and the Eh values are higher for site A (56.4 % < [O₂] saturation < 81.1 %; 166 mV < Eh < 270 mV) than for site B (1.4 % < [O₂] saturation < 27.3 %; -2 mV < Eh < 271 mV). The dysoxic conditions of site B should favor the transfer of Fe and Mn from oxides-hydroxides or amorphous / colloid phases located in the sediment to "free metal ions" in the pore water in which watercress roots acquire their nutrients. This trend is more pronounced for Mn than for Fe, in accordance with the redox cascade pattern generally described for natural waters (Stumm and Morgan, 1996). For site B the average Mn concentration in watercress increased by a factor 7.5 but the Fe concentration only increased 2.2 times compared to site A.

If the ion metal speciation status explains the difference in watercress Mn and Fe concentration levels between the two sites, there must be Fe and Mn, either available in the sediments or transferred from the local riparian zones. Availability in the sediments (exchangeable and potentially exchangeable fractions) may be assessed using the results of the selective extractions (Table 4). Bottom sediments of site B do contain more Fe bound to oxides-hydroxides (potentially exchangeable Fe) than for site A,

10.0 - 24.0 g kg⁻¹ vs. 2.2 - 5.7 g kg⁻¹, respectively. For Mn, the same trend was observed with 4.2 - 20.4 g kg⁻¹ and 0.9 - 2.4 g kg⁻¹ for site B and A, respectively. Accordingly, sediments contain more Fe and Mn in site B than in site A and the concentrations measured in watercress may be explained by differences in sediment composition. Differences in sediment composition between each site are highlighted by their TOC content (Table 4). Organic matter is well preserved in the swampy area of site B with high TOC concentrations (23.9 - 63.2 mg C g⁻¹). In contrast, site A bottom sediments have lower organic carbon contents (9.1 - 37.2 mg C g⁻¹). Nevertheless, improved preservation of vegetation debris in dysoxic - suboxic conditions with reduced mineralization rates or simply removal of organic debris by stream flow may also explain this difference. Local environmental control is suggested by the contrasted exchangeable Fe- and Mn- concentrations measured for each sites. The proportion of exchangeable Mn at site B was higher at 0.216 - 0.475 g kg⁻¹ than for site A, at 0.003 - 0.067 g kg⁻¹. This was not the case for Fe at site B where the exchangeable Fe-concentrations are in the same range as that observed for site A. The differential behavior of Fe and Mn (with respect

to local environmental conditions) is supported by the calculated partition coefficients (K ; ratio of exchangeable vs. potentially exchangeable concentrations, Table 4). Thus, for Mn in site B a higher rate of exchange between bottom sediments and water is possible whereas only low exchange is expected for Fe. This pattern is also consistent with the redox trends reported for natural waters (Stumm and Morgan, 1996). Overall, both local sediment composition and prevailing environmental conditions explain the difference in the Fe- and Mn-contents of watercress.

Fe and Mn concentrations in ambient water

Because stream waters on the Houay Pano catchment have high pH and low turbidity during the dry season, dissolved Fe- and Mn-concentrations should be very low. High metal concentrations in surface waters are not favored by high pH conditions and the turbidity in the watercress cultivation area is too low to provide particulate sources of metals. Some limitations to our assessment were caused by a local groundwater inflow located at site A (sample A4* in Table 1 - 2). The pH of this groundwater inflow was lower (6.47) than for ambient stream waters (7.49 - 7.94) and the

dissolved oxygen concentration were also much lower (11 % at saturation). Major differences were also found between the two water sampling and analysis procedures. Dissolved Fe and Mn concentrations were either in the same range or higher using direct DGT recovery than after water filtration (Table 2). The opposite trend should be found because with the former method only "free metal ions" should be recovered whereas with the later method the dissolved component may contain colloid fractions and possibly also very fine particulate matter ($< 0.2 \mu\text{m}$). This unexpected behavior indicates that removal of Fe and Mn from the dissolved load with concomitant precipitation of Fe-Mn oxides and hydroxides on the acetate filter took place during water filtration. In order to reduce uncertainty, we decided to only use the concentrations obtained using the DGT procedure when referring to dissolved element concentrations.

The distribution of dissolved Fe- and Mn- concentrations in ambient water mirrored the trends obtained for watercress and exchangeable metals in sediments. High dissolved Fe and Mn contents in ambient water correspond to high concentrations in watercress and bottom sediments. For example, at site B, watercress samples B2 - B5

have “high” Mn content (21.1 - 26.6 g kg⁻¹, Table 3), the corresponding bottom sediments have “high” exchangeable Mn-concentrations (0.216 - 0.475 g kg⁻¹, Table 4) and ambient water has a “high” dissolved Mn content (1404.1 - 4359.3 µg l⁻¹, Table 2). In contrast, watercress samples A2 - A3 and A5 - A10 from site A with a “low” Mn content (1 - 10 g kg⁻¹, Table 3) are linked to “low” exchangeable Mn-concentrations in sediments (0.003 - 0.067 g kg⁻¹, Table 4) and “low” Mn levels in ambient water (13.1 - 53.2 µg l⁻¹, Table 2). The local groundwater inflow at site A (sample A4*, Table 2), characterized by contrasting redox conditions as mentioned above, has a slightly higher dissolved Mn-concentration (480 µg l⁻¹, Table 2) consistent with the more reducing conditions (lower dissolved oxygen and redox potential levels) of ground waters. Additional evidence for a consistent behavior between ambient water, watercress and bottom sediment was displayed by the dissolved Fe-concentrations which were higher for site B than for site A, as already shown for watercress Fe-contents and sediment potentially exchangeable Fe-concentrations. However, locally more reducing conditions also occurred. Water samples B7 - B9 (Tables 1 and 2) collected in a confined part of site

B, where watercress no longer grows, displayed an opposite trend with much higher amounts of dissolved Fe (4384.0 - 8556.7 µg l⁻¹, Table 2) with respect to dissolved Mn (264.2 - 1828.1 µg l⁻¹, Table 2). These concentrations were consistent with very low dissolved oxygen content of these waters (1.4 % < [O₂] saturation < 3.2 %).

Conclusion and perspectives

Analysis of Fe and Mn-concentrations in watercress, bottom sediment and ambient water for two sites with contrasted environmental conditions (oxic vs. dysoxic - suboxic oxygen levels) showed that metal accumulation levels are linked to the local bottom sediment composition and local environmental conditions (composition of soil waters). The levels of Fe and Mn accumulated in the watercress were high due to the ability of roots to directly take up soluble metals (“free ion”) from soil water. Higher levels of Mn were observed in watercress grown in the swampy area compared to the upstream site, which is consistent with both the higher exchangeable Mn-concentrations in the bottom sediments and the higher dissolved Mn-content of stream waters measured at the site. Higher Mn availability is also expected

according to the local redox status. A high level of Fe-accumulation in watercress was not favored by the local conditions recorded during the course of this study but might have taken place previously when more reducing conditions prevailed during the dry season. An important outcome of this study is that the total Fe and Mn accumulations in watercress cultivated in the swampy area (site B of our study) might reach and even exceed the levels reported in metal contaminated sites.

The bioaccumulation of these metals should not pose a direct threat in itself, because these elements are not actually very toxic, but rather it is indicative of the local physico-chemical conditions that could be potentially favoring the mobility and accumulation of toxic metals such as the so-called atmophile elements (e.g. Cu, Cd, Zn, As). These elements are the subject of an ongoing study. Because watercress appears to effectively take up and accumulate metals it could be used to clean up contaminated waters as a bioremediation component.

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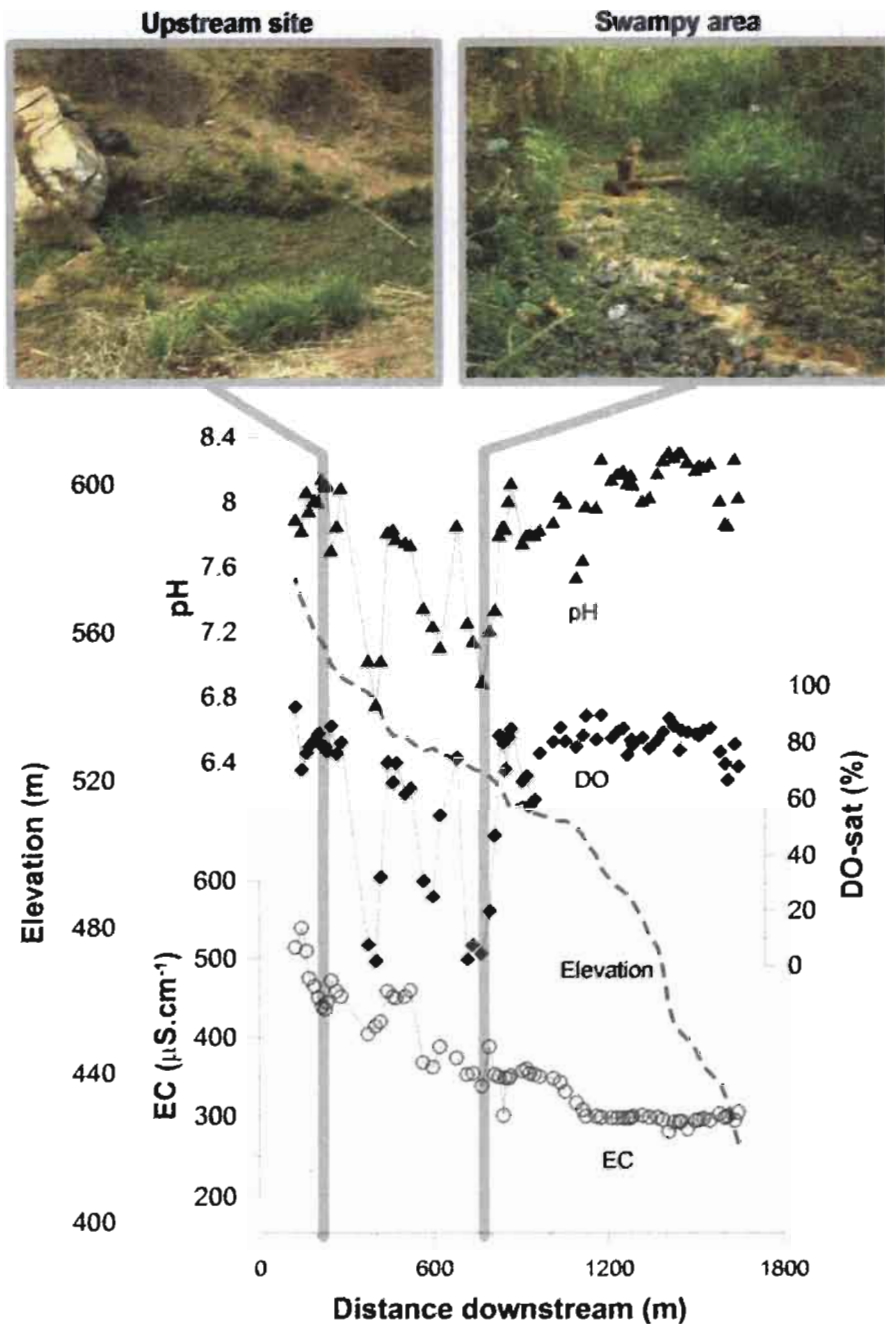


Figure 1 – Pictures showing the upstream site and the swampy area; Elevation and physicochemical characteristics along the Houay Pano stream during the sampling collection (5 March 2007): pH, dissolved oxygen content transformed to oxygen saturation (DO-sat) and electrical conductivity at 25°C (EC).

Table 1 – Major environmental parameters measured on the day of the sampling.

Sample	Water Temperature (°C)	Water EC ($\mu\text{S}\cdot\text{cm}^{-1}$)	pH	Eh (mV)	[O ₂] % saturation	[O ₂] (mg.l ⁻¹)
Site A (upstream)						
A1	21.90	534	7.49	166	63.0	5.5
A2	22.34	541	7.54	186	61.5	5.3
A3	23.16	544	7.75	205	65.8	5.6
A4 *	19.53	177	6.47	270	11.0	1.0
A5	23.12	525	7.83	235	70.1	6.0
A6	22.67	517	7.48	244	71.1	6.1
A7	23.12	512	7.58	247	63.6	5.4
A8	23.73	502	7.94	247	81.1	6.9
A9	23.67	501	7.65	252	56.4	4.8
A10	23.58	496	7.97	248	80.4	6.8
Site B (swampy area)						
B1	21.27	371	7.11	271	27.3	2.4
B2	20.30	363	7.03	179	6.0	0.5
B3	20.61	379	7.07	184	16.7	1.5
B4	19.64	378	7.05	169	8.5	0.8
B5	19.34	381	7.19	214	14.3	1.3
B6	18.77	388	7.14	120	18.6	1.7
B7	19.09	382	6.94	104	2.0	0.2
B8	18.55	441	7.23	-2	1.4	0.1
B9	19.21	351	6.83	117	3.2	0.3

* local groundwater inlet

Table 2 – Fe- and Mn- concentrations measured in water samples after filtration and using the DGT procedure.

Samples	Filtration [Fe] ($\mu\text{g l}^{-1}$)	Filtration [Mn] ($\mu\text{g l}^{-1}$)	DGT [Fe] ($\mu\text{g l}^{-1}$)	DGT [Mn] ($\mu\text{g l}^{-1}$)
A1	4.4	bd	11.9	2522.2
A2	-	-	4.5	53.2
A3	bd	3.3	6.2	13.1
A4*	3.9	bd	10.9	480
A5	bd	bd	-	-
A6	bd	bd	5.8	2.7
A7**	bd	bd	15.0	49.1
A8	bd	bd	4.5	4.1
A9	7.0	bd	-	-
A10	24.6	bd	2.7	42.4
B1	1.2	200	5.6	2620.1
B2	2.4	190	955.8	1404.1
B3	1.0	220	62.8	4359.3
B4	bd	190	80.6	2156.1
B5**	bd	200	50.7	3553.0
B6	1.3	170	9.0	1983.5
B7	4.6	720	4384.0	1828.1
B8	6.1	340	8556.7	341.2
B9	bd	54	4848.0	264.2

* local groundwater outlet, ** average of 2 replicate samples, bd = below detection limit

Table 3 – *Fe- and Mn-concentrations measured in dry watercress samples (average of 2 replicate samples).*

Samples	Water content (weight %)	[Fe] (g kg ⁻¹)	[Mn] (g kg ⁻¹)
A1	96.2	4.4	2.0
A2	93.7	10.0	10.0
A3	94.8	6.1	2.0
A5	93.0	12.8	1.2
A6	91.1	14.7	1.0
A7	95.0	15.0	7.3
A8	94.7	18.6	1.7
A9	93.9	15.2	1.5
A10	95.1	19.6	2.2
B2	96.4	14.1	26.6
B3	96.4	28.4	22.0
B4	96.4	46.5	26.6
B5	95.8	26.9	21.1

Table 4 – Total organic carbon, total nitrogen, TOC/TN (= C/N), Fe and Mn-concentration measurements for sediment samples using selective extractions and partition coefficients (K) of exchangeable vs. potentially exchangeable Fe and Mn. (Exchan. = exchangeable = CaCl₂ treatment, oxides = potentially exchangeable = HNO₃ + HCl treatment).

Samples	TOC (mgC. g ⁻¹)	TN (mgN. g ⁻¹)	C/N	Exchan. [Fe] (mg.kg ⁻¹)	Exchan. [Mn] (g.kg ⁻¹)	[Fe] oxides (g.kg ⁻¹)	[Mn] oxides (g.kg ⁻¹)	K (Fe) (x 10 ⁶)	K (Mn) (x 10 ³)
A1	12.2	1.4	8.7	bd	0.020	5.7	0.9	-	22.7
A2	22.3	2.3	9.7	0.052	0.067	5.6	1.8	9.4	36.4
A3	23.2	2.1	10.9	0.026	0.009	2.9	1.3	9.1	6.7
A5	18.7	1.8	10.3	bd	0.006	3.6	1.4	-	3.9
A6	17.5	1.7	10.5	bd	0.008	4.2	1.4	-	5.9
A7	37.2	2.9	12.8	0.021	0.003	2.2	2.4	9.3	1.3
A8	25.0	2.1	11.7	0.039	0.036	3.1	2.1	12.7	17.1
A9	16.0	1.5	10.5	0.018	0.003	3.6	0.9	5.0	3.5
A10	9.1	0.9	10.1	bd	0.002	4.6	0.9	-	2.1
B2	53.2	3.7	14.5	0.071	0.289	17.1	9.9	4.1	29.1
B3	41.4	3.0	14.0	0.027	0.359	18.8	11.5	1.4	31.3
B4	63.2	3.9	16.4	0.041	0.475	24.0	20.4	1.7	23.3
B5	23.9	1.9	12.9	0.014	0.216	10.0	4.2	1.5	51.7

bd = below detection limit

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