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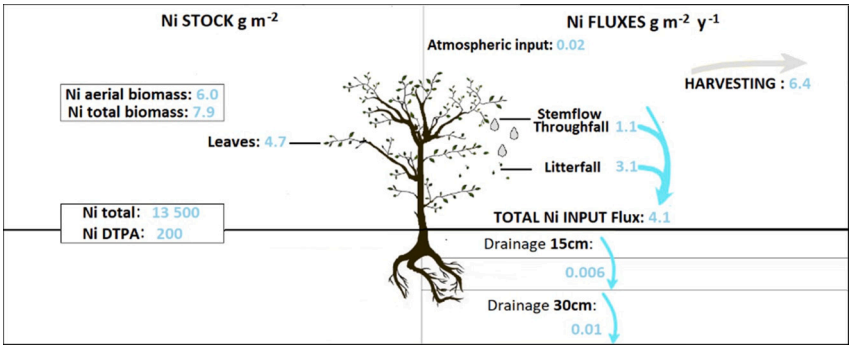
HIGHLIGHTS

- Nickel cycle was mainly driven by internal fluxes.
- After two years of cropping, the Ni litter flux corresponded to 50 % of the total Ni stock in the aerial biomass.
- The stability of the Ni available pool in soil could be due partly to the Ni return by litterfall.
- Sustained agromining would lead to a depletion of Ca stocks.

GRAPHICAL ABSTRACT



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ABSTRACT

Nickel hyperaccumulator plants play a major role in nickel recycling in ultramafic ecosystems, and under agromining the nickel dynamics in the farming system will be affected by removal of nickel-rich biomass. We investigated the biogeochemical cycling of nickel as well as key nutrients in an agromining operation that uses the metal crop *Phyllanthus rufuschaneyi* in the first tropical metal farm located in Borneo (Sabah, Malaysia). For two years, this study monitored nine 25-m^2 plots and collected information on weather, biomass exportation, water, and litter fluxes to the soil. Without harvesting, nickel inputs and outputs had only minor contributions (<1 %) to the total nickel budget in this system. The nickel cycle was mainly driven by internal fluxes, particularly plant uptake, litterfall and throughfall. After two years of cropping, the nickel litter flux corresponded to 50 % of the total nickel stock in the aerial biomass (3.1 g m^{-2} $year^{-1}$). Nickel was slowly released from the litter; after 15 months of degradation, 60 % of the initial biomass and the initial nickel quantities were still present in the organic layer. Calcium, phosphorus and potassium budgets in the system were negative without fertilisation.

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Unlike what is observed for nickel, sustained agromining would thus lead to a strong depletion of calcium stocks if mineral weathering cannot replenish it.

1. Introduction

Hyperaccumulator plants have evolved specific molecular and physiological mechanisms to accumulate and tolerate certain trace elements to extremely high concentrations in their living shoots when compared to plants growing on the same substrates (Jaffré et al., 1976; Reeves, 2003; van der Ent et al., 2013). More than 700 hyperaccumulator plant species are currently reported globally, of which >500 taxa hyperaccumulate nickel (Ni) (Reeves et al., 2017). In order for a plant to be classified as a Ni hyperaccumulator, it has to accumulate >0.1 wt% (i.e., >1000 mg kg^{-1}) of Ni in its shoots (Baker and Brooks, 1989; van der Ent et al., 2013). Nickel hyperaccumulators are mostly restricted to ultramafic soils globally; these soils have particularly low concentrations of essential nutrients (such as K and P), but relatively high concentrations of trace elements (Cr, Co, Mn, and Ni) (Echevarria, 2018; Proctor, 2003).

Hyperaccumulator plants are increasingly being studied for their potential use in Ni recovery from the soil (e.g. Nascimento et al., 2022). Agromining is a chain of processes where selected hyperaccumulator plants are cropped and harvested to recover a high-grade bio-ore (Angle et al., 2007; Barbaroux et al., 2011; Nkrumah et al., 2018a). To be used for agromining, selected hyperaccumulators ('metal crops') need to have a high biomass production and an ability to accumulate >1 wt% Ni in their aerial biomass (Angle et al., 2007; Nkrumah et al., 2016, 2018a). Agromining could rehabilitate mining soils and provide an alternative for agriculture on degraded soil, which has the potential to significantly improve the livelihood of local farmers (Erskine et al., 2018; van der Ent and Mulligan, 2015). There are significant untapped opportunities for the economic exploitation of Ni agromining in the tropics (Nkrumah et al., 2021; Nkrumah et al., 2019d; Paul et al., 2021). To date, five potential 'metal crops' have been reported from Sabah (Malaysia), including *P. rufuschaneyi* (Bouman et al., 2018; Nkrumah et al., 2019a, 2019b).

Agronomic systems play a significant role in developing sustainable Ni agromining (Bani et al., 2014; Nkrumah et al., 2018b, 2021). Moreover, the first tropical agromining farm has been set up in 2016 in Pahu, Sabah, Malaysia (Nkrumah et al., 2019a, 2019b, 2019c) to provide real life evidence of tropical Ni agromining, and a model for further studies. In the field trial, Ni yield was estimated to reach 250 kg ha^{-1} using a plant density of four *P. rufuschaneyi* per m^2 (Nkrumah et al., 2019d). However, a Ni yield of only 75 kg ha^{-1} was obtained in the field with the same plant species (Tisserand et al., 2021) employing two plants per square meter. There are significant knowledge gaps that require investigations to optimise tropical Ni agromining in the field (Nkrumah et al., 2021). Firstly, the threshold of available Ni concentrations required for optimum plant uptake and shoot Ni accumulation is unknown. Secondly, the number of cropping years required to deplete the available Ni pool has remained unexplored. Thirdly, the role of subsoil Ni in replenishing the available Ni pools in the topsoil needs investigation. In addition, the effect of harvesting Ni rich biomass on the nutrient pools in the topsoil also remains unknown. Hence, detailed studies on Ni (and other elements) biogeochemical cycles could help address some of these knowledge gaps and contribute to the development of robust agronomic systems for sustainable tropical Ni agromining.

The mobility and accumulation of Ni and other metals can be influenced by different parameters including soil organic matter, Fe and Mn oxides (Alves et al., 2011; Bani et al., 2014; Kalbitz and Wennrich, 1998). In ultramafic soils, Ni behaviour is mainly controlled by soil pH and soil Ni-bearing phases (Echevarria et al., 2006). Previous studies have investigated the local soil chemistry and foliar elemental concentrations in tropical hyperaccumulator plants (van der Ent and Mulligan, 2015; van ver Ent et al., 2015; van der Ent et al., 2016, 2018a, 2018b), but hyperaccumulator litter degradation has received little attention. For the temperate Ni 'metal crop' *Odontarrhena chalcidica*, leaf Ni leaches rapidly after decaying (Echevarria, 2021). Hyperaccumulator plants are responsible for a significant part of the available Ni in topsoil due to Ni rich leaf litter recycling (Echevarria et al., 2018; Estrade et al., 2015; Paul et al., 2021; Ratié et al., 2019; Tisserand et al., 2022; Zelano et al., 2020). Large quantities of Ni having biotic origin are found in the upper soil layer of hyperaccumulator forests (Zelano et al., 2020). Sustained harvesting could deplete quantities of available Ni; nevertheless, this process could also promote the transfer of non-labile soil Ni to phytoavailable forms.

This study aims at assessing and understanding the fluxes (i.e., the internal system stocks and turnover) of Ni and other elements in a tropical 'metal crop' system at the Pahu Agromining Trial Farm in Sabah, Malaysia. Therefore, nine different *P. rufuschaneyi* homogeneous mono-cropping instrumented plots were assessed thanks to the control of litter return after regular coppicing of plant shoots: (i) normal return of litter to the soil, (ii) double return with twice the amount of litter of the normal system, and (iii) no return due to full exportation of the plant biomass after coppicing (correspond into an 'agromining scenario'). Each treatment consisted of three replicated plots. To that end, the concentrations and annual fluxes of Al, Ca, Fe, K, Mg, Na, Ni, P and S were measured in the trial plots in the metal farm. Total and available stock of these elements in soils and plants were also studied.

2. Materials and methods

2.1. Study location and plant species studied

This study was undertaken at the Pahu Agromining Trial Farm (Nkrumah et al., 2019a; Tisserand et al., 2021) close to Pahu village, North Borneo, Sabah, Malaysia (335 m asl, 6°7′49″N;116°46′22″E). This ultramafic Eutric Chromic Cambisol has already been described (Nkrumah et al., 2019a; Tisserand et al., 2021). *Phyllanthus rufuschaneyi* is cultivated at this site due to its highly desirable traits for agromining, including high shoot Ni concentrations with up to 3.2 wt% in old leaves, rapid re-growth after coppicing, tolerance for exposed conditions and pest resistance (Bouman et al., 2018; Nkrumah et al., 2019b; Tisserand et al., 2021; van der Ent and Mulligan, 2015; van der Ent and Mulligan, 2015). For this experiment, *P. rufuschaneyi* saplings were collected in their native habitat and transplanted into polyethylene bags containing ultramafic soil in a shade house. The soil used for transplanting saplings was homogeneous topsoil from the Pahu ultramafic field (Nkrumah et al., 2019a; Tisserand et al., 2021). Transplantation into the field plots occurred in February 2018 with plants of 25 (± 8) cm height; nine 25 m^2 plots were planted at a density of two scrubs per square meter.

2.2. Experimental treatments applied in the system

In November 2018, an initial homogeneous NPK fertilisation (370 kg ha^{-1}) was applied to avoid nutrient limitation before the application of the organic treatment. Starting from November 2018, hyperaccumulator plants were amended with litter four times with three replicates. A control treatment was put in place. Every four months, two different rates of litter: 250 or 500 g m^{-2} were applied, until a complete treatment application of 1 kg m^{-2} for the lowest dose and 2 kg m^{-2} for the highest dose were achieved in November 2019 (Fig. S1). The lowest dose corresponds to the amount of litter measured in a natural ultramafic forest dominated by *P. rufuschaneyi* (Tisserand et al., 2022). These litter treatments consisted of *P. rufuschaneyi* shoot biomass crushed with a

shredder (Tisserand et al., 2021) and composed of 1 wt% Ni, 0.8 wt% K, 0.7 wt% Ca and 0.6 wt% P. Litter bags, with small mesh (20 × 20 cm; 1 mm mesh), were laid on the soil surface in all plots at each treatment application to be able to follow the litter degradation. The mesh size of the nylon bags prevented loss of small leaf fragments but allowed access by bacteria, fungi, and small soil invertebrates.

2.3. Biogeochemical station installation

In March 2018, a biogeochemical station was installed in the plot (Fig. S2). A weather station, gutters, stemflow collectors, lysimeter and litter traps were randomly positioned at each subplot to monitor the following fluxes: rainfall, throughfall, stemflow and gravity water. These samples were collected every two weeks for surface water and every month for gravity water at a minimum. Gravity water samples were collected before each treatment at 15 cm and 30 cm depth. Nine litterfall collectors with a surface area of 0.25-m^2 were installed 10 cm above ground level. Agronomic parameters measurement (stem diameter, plant height, number of stems) and litter collection were scheduled every month.

2.4. Soil collection and chemical analyses

Soil was collected eight months after planting; four soil cores of 10-cm diameter were collected in each subplot before treatment (depth: 0–5 cm, 5–10 cm, 10–15 cm). Two pits were dug up to the transitional horizon in January 2020 to collect soil samples along the soil profile (Fig. S1). The soil profile was divided according to the number of visible horizons (top-soil: A11 and A12, accumulation horizon: Bw and degradation horizon: BC). The soil pH was measured after solid suspension of dry soil sieved at 2 mm with deionised water at a ratio of 1/5 (m/v) (NF ISO 10390). Bioavailable nutrients and metals were extracted using hexaamminecobalt(III) trichloride (ISO/DIS 23470) and diethylene triamine pentaacetic acid (DTPA) (NF ISO 31- 121), respectively. The soil pseudo-total concentrations were determined by using Aqua Regia by digesting 0.5 g of each soil sample with 2 mL HNO_3 and 6 mL HCl for 2 h at 95 °C before filtration and analyses with ICP-OES (Thermo Fisher iCAP 6300 Duo). For all the protocols, blanks and standard reference materials were analysed.

2.5. Biomass measurement and litter analyses

One year after the initial treatment application, 12 plants per treatment were collected in January 2020. Plants were separated into different fractions after washing the roots with ultrapure water (roots, stems and leaves). Stems and leaves were analysed separately in the lignified part of the plants (old) or non-lignified part of the plants (young). Samples were dried for 48 h at 40 °C prior to grinding. Pseudo-total element concentrations were determined in plant samples after digestion for 16 h with 1 mL HNO_3 (70 %) and 2 mL H_2O_2 (30 %) at room temperature after which the samples were heated for 2 h at 95 °C in a DigiPREP® system for 120 min at 95 °C prior to filtration 0.45 µm (Millipore). Each solution was analysed with ICP-OES (Thermo Fisher iCAP 6300 Duo). The recovery rates for Ni varied between 90 and 110 %. Tree litter bags were collected from the treated plots at 1, 2, 4, 8 and 15 months. After collection, each bag was dried and separated (leaves, petioles, wood, and dust) and then weighed. Litter bags samples were analysed with the same protocols for plant samples presented in the previous paragraph. To measure soil contamination at each litter sampling, at each time of litter bag collection composite samples of each plant organ were heated in muffle furnace at 550 °C for three hours to remove entirely organic matter. After cooling to room temperature overnight, the samples were reweighed to calculate mass loss.

2.6. Water measurement and chemical analyses

After collection, water samples (rainfall, throughfall, stemflow and gravity water) were filtered at 0.45 µm and stored refrigerated (~4 °C) until analysis. Samples for total element analyses were acidified (0.5 %) with ultrapure HNO3 before analysis with ICP-OES (Thermo Fisher iCAP 6300 Duo).

2.7. Calculations of the elemental fluxes and litter degradation

Starting in March 2018 until January 2020, total rainfall (TR) was 3720 mm (mean of ~2180 mm per year) and a mean temperature of 24.9 ± 0.6 °C. Atmospheric deposition was calculated using elemental concentrations in the rainfall (DD). Stemflow, throughfall and litter fluxes were calculated considering the average density of two plants per square meter. Total nutrient input (It) was calculated by adding the quantities of nutrients in litterfall (Lf), stemflow (Sf) and throughfall (Tf): It = Sf + Lf + Tf-DD [g m^{-2} y^{-1}]. The total nutrient output was calculated by adding the quantities of nutrients in gravity waters at 30 cm depth (GW) and in harvested biomass (HB): Ot = GW + HB [g m^{-2} y^{-1}], The annual budget (AB) was calculated by subtracting nutrient output to nutrient input: AB=It – Ot [g m^{-2} y^{-1}], In the litter degradation experiment, the decomposition rate constant (Olson, 1963) (k) was calculated by subtracting weight at the time, t (Wt) from weight at the initial time (W0) and dividing by time, t in y^{-1}: k = (W0-Wt)/t. The Ni percentage remaining in litter bags (Nirem) was determined by dividing Ni quantity at the time of collection (Nit) by initial Ni quantity (Ni0): Nirem = (Nit /Ni0)*100 [%]. The Ni litter degradation flux is calculated by using the quantity of Ni applied per square meter (Nitreat): NiLD = (1-(Nirem/100))*Nitreat [Ni mg m^{-2}]. The internal cycle of the plants, nutrient and metal remobilisation before senescence was calculated from the difference of concentrations in leaves in place and leaf litter: (Clitter-Cleaves)/Cleaves*100 [%], The impact factor on biochemical cycles, translocation factor (TF) was measured by dividing elemental concentrations in shoots by roots: TF = Cshoot/Croots.

2.8. Statistical analysis data

Statistical analyses were performed using R software, version 3.6.2 (2019-12-22). The significant difference between treatments was tested using Kruskal-Wallis test with a confidence level of 95 %. Post-hoc pairwise comparisons were performed using Dunn's test.

3. Results

3.1. Elemental concentrations and stocks in soils of the system

Pseudo-total nickel concentration varied along the soil profile (Table 1, S1). In the first pit, Ni concentration was lower in the A11 (4100 mg kg^{-1}) than A12 horizon (4900 mg kg^{-1}), whereas in the second pit, Ni concentration was constant between these two horizons (5100 mg kg^{-1}). Although the pseudo-total Ni concentration of the latter

Table 1
Total and Ni DTPA concentrations in mg kg^{-1} of the two pits of Pahu field in January 2020 and of the plot soils from 0 to 15 cm depth in November 2018 before first litter treatment (0 or 2 kg m^{-2} of litter). For averages that are the same between treatments, only one value is shown (n = 3).

		Mn	Ni	Ca	K	Mg	Ni DTPA
$A1_1$	I	6100	4100	4800	160	50,000	110
	II	7300	5100	4500	600		
$A1_2$	I	6300	4900	3400	60	55,000	70
	II	6700	5100	4000	110		130
B	I	3700	8700	2200	110	60,000	90
	II	2700	6400	2300	40		100
C	I	2300	6600	1200	40	62,000	94

was constant, its DTPA-extractable Ni concentrations increased from 110 mg kg^{-1} in A11 to 130 mg kg^{-1} in A12. For the first pit, DTPA-extractable Ni decreased from 110 mg kg^{-1} in A11 to 70 mg kg^{-1} in A12. B horizon had the highest pseudo-total Ni concentrations in both pits (Table 1). The Mg concentration did not vary between the two pits but increased from 50 g kg^{-1} at the surface to 70 g kg^{-1} at BC horizon. However, Ca concentrations had an opposite trend to Mg (Table 1). Potassium decreased with depth, from 160 to 40 mg kg^{-1} in the first pit and 600 to 30 mg kg^{-1} in the second pit (Table 1). In the spatial distribution, K varied strongly in the topsoil (160 and 600 mg kg^{-1}) compared to the BC horizon (40 and 30 mg kg^{-1}), in pits 1 and 2, respectively. The elemental concentrations in the surface soil (0–5, 5–10 and 10–15 cm) of each plot are presented in Tables 2; S2; S3; S4; S5. In the 0–5 cm soil depth, Ni increased (1.2-fold) in the 2 kg m^{-2} litter treated plot compared to the control (p 0.08) (Table 2). Phosphorus, S, K and Ca increased by 1.9-, 1.5-, 2.8- and 1.3-fold, respectively, compared to the control ($p < 0.05$). However, Mn concentrations were relatively higher in the control (4800 mg kg^{-1}) relative to the treated plot (4200 mg kg^{-1}) ($p = 0.04$). In the 10–15 cm soil depth, only K concentration was statistically higher in the treated plot compared to the control ($p = 0.03$). In January 2020, Ni available stock in the surface soil was 52 g m^{-2} for control, and 100 g m^{-2} for litter treated soil. Ni stock in the surface soil was 2.4 kg m^{-2} for control and 2.3 kg m^{-2} for litter treated soil (Table 2). Notably, Ni is the third highest stock, after Cr (2.5 kg m^{-2}) and Mg (1.8–2.1 kg m^{-2}).

3.2. Elemental concentrations and stocks in plants

Nickel concentrations in *P. rufuschaneyi* varied significantly in the plant fractions ($p < 0.01$) but did not vary between control and litter treatments (Fig. 1; Tables S6, S7). The leaves had the highest Ni concentrations, reaching 3.2 and 3.4 wt% in old and young leaves, with mean concentrations of 22,000 mg kg^{-1} (2.2 wt%) and 19,000 mg kg^{-1} (1.9 wt%), respectively (Fig. 1). The primary roots were relatively enriched in Ni compared to old stem (1.6-fold) ($p < 0.05$); the old stems had the lowest Ni concentrations relative to all plant parts (Fig. 1). Calcium and K were relatively enriched in the leaves, with 7000 mg kg^{-1} (0.7 wt%) and 6000 mg kg^{-1}(0.6 wt%) in the control treatment and 10,000 mg kg^{-1} (1.0 wt%) and 8000 mg kg^{-1} (0.8 wt%) in the litter treatment, respectively, compared to Mg (Table 2). The leaves consisted of 60 % the total tree biomass and 80 % of the tree aerial biomass. Almost two years after planting, the Ni stock in the *P. rufuschaneyi* in the

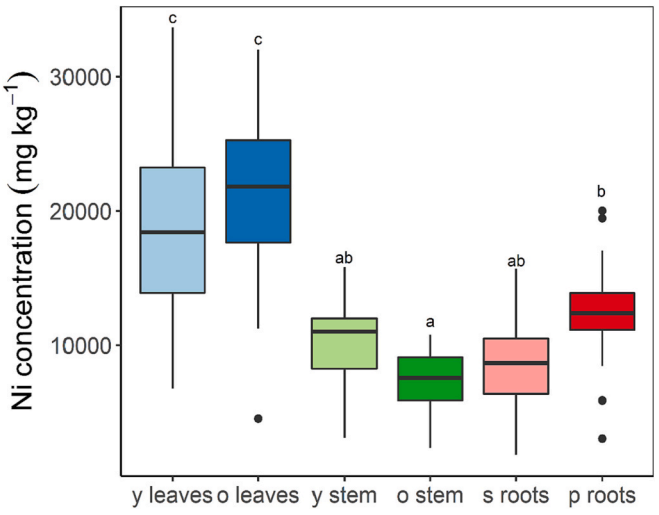

Fig. 1. Nickel concentrations in the different parts of *Phyllanthus rufuschaneyi* in January 2020. Differences between plant organs are indicated with lowercase letters ($p < 0.05$) (y = young; o = old; s = secondary; p = primary) (means ± standard deviation; $n = 27$).

Table 2
Elemental stocks in soils surface and plants (roots; stems; leaves) in g m-2 in January 2020. Only means followed by letter are significantly different ($p < 0.05$ level) (n = 3). For averages that are the same between treatments, only one value is shown.

			Litter kg m^{-2}	Cr	Mn	Ni	Zn	Ca	K	Mg	Na	P	S
Concentration mg kg^{-1}	Young leaves		0	30	230	19,000		6100	7000	3500	–	1000	2400
			2		250			8800	8400	3300		1200	1900
	Young stem		0		490	10,000		9900	14,000	2500		2500	2300
			2		900	12,000		13,000	16,000	2700		3300	300
	Leaves		0		240	20,000	190	7000	6400	3300		880	2300
			2					9600	7500	3100		940	2500
	Stem		0	20	80	7400	80	6900	9400	1400	310	1700	1500
			2	40		7800		10,000	10,000		440	2100	2900
	Roots		0	150	120	11,300	120	5000	5300	3300	490	730	1400
			2	330	210	10,600		6000	5500	4600	660	660	
	Soil Pseudo-Total	0-5 cm	0	6400	4800b	5400	110	2800	140a	47,000	40a	150a	190a
			2	6300	4200a	6500	110	3500	390b	43,000	150b	280b	280b
		5–10 cm	0	7100	5600b	6400	120	4000	110a	61,000	50	120a	210
			2	5700	4500a	5900	100	3000	250b	47,000	50	160ab	220
		10-15 cm	0	6700	4900	5900	120	3600	90a	55,000	40	82a	180
			2	6100	4400	5900		3200	220b	50,000	60	175b	230
Stock g m^{-2}	Young leaves		0	–	0.01	1.1	0.01	0.4	0.4	0.2	–	0.07	0.1
			2		0.02	1.5		0.7	0.8			0.1	0.2
	Young stem		0		0.002	0.2	–	0.2	0.2	0.02		0.05	0.05
			2					0.3	0.3	0.05		0.07	0.05
	Leaves		0		0.07	5.4	0.05	1.9	1.6	0.8		0.2	0.6
			2		0.06	5.3		2.5	2.0			0.6	0.5
	Stem		0		0.02	1.4	0.01	1.7	1.8	0.2		0.4	0.3
			2		0.01	2.0		2.4	2.5	0.2		0.6	0.4
	Roots		0	0.02	0.02	2.0	0.02	0.8	1.2	0.4	0.05	0.2	0.3
			2			3.0		1.9	0.7	0.5	0.2		
	Plant		0	0.02	0.08	8.7	0.02	3.8	3.6	1.2	0.10	0.7	0.9
			2		0.09	9.7		6.2	5.2	1.3	0.25	0.9	1.3
			0			2400		1300	110	18,000	40	90	90
		Total 0-15 cm	2	2500	1800	2300	40	1400	60	21,000	20	50	80
			0		27	52							
	Soil	DTPA 0-15 cm	2	–	24	100	0.2						

Table 3
Elemental fluxes in g m^{-2} y-1 from January 2019 to January 2020.

Litter	Quantity flux (g m-2 y-1)	Mn	Ni	Zn	Ca	K	Mg	Na	P	S
0 kg m-2	Dry Deposit	0.01	0.02	0.09	0.7	0.25	0.3	0.4	0.01	17
	Fertilisation*	–	–	–	–	5.4	–	–	5.4	–
	Throughfall	0.12	1.1	0.04	1.4	2.1	1	0.35	0.04	40
	Stemflow	–	0.004	–	0.02	0.01	0.005	0.003	0.001	0.2
	Litterfall	0.03	3.0	0.02	0.58	0.13	0.23	–	0.03	0.08
	Total nutrient return	0.16	4.1	0.15	2.7	7.9	1.5	0.75	5.5	57
	Drainage	–	0.01	–	0.25	0.11	1.2	0.06	–	4.3
	Harvesting	0.12	6.4	0.05	3.2	1.8	0.8	0.06	0.6	0.8
	Total nutrient loss	0.12	6.4	0.05	3.45	1.91	2	0.12	0.6	5.1
	Total soil annual budget	−0.11	−2.3	0.1	−0.75	6.0	−0.47	0.63	4.9	52
2 kg m-2	Total nutrient return	0.12	3.8	0.20	3.1	8.4	1.4	0.74	5.5	69
	Total nutrient loss	0.12	6.4	0.05	3.75	1.85	1.3	0.11	0.6	6.1
	Total soil annual budget	–	−2.6	0.15	−0.68	6.6	0.12	0.63	4.9	63

control plot was 8.7 g m^{-2}, with 6.7 g m^{-2} in aerial biomass out of which 5.3 g m^{-2} was in the leaves (Table 3). For plants amended with litter, the Ni stock was slightly higher (9.7 g m^{-2}) but not statistically significant. Nickel had the highest stock in biomass relative to all the elements, followed by Ca and K (Table 2).

3.3. Water fluxes in the system

Mean concentrations of ions in precipitation, throughfall, stemflow and gravity water are shown in Fig. 2. Statistical variations between treatments were significant for some elements (Ca, K, Mn, Na, Ni and P) and some instruments. Drainage was estimated using gravity water volume and concentration in elements at 30 cm. It was higher for Ca and Na for the higher litter treatment. Tendencies of Fe loss in the highest dose treatment (2 kg m^{-2} of litter) was measured (p 0.13). Throughfall and stemflow concentrations were higher than in lysimeter waters for K, Mn, Ni, P and Zn ($p < 0.01$). The concentrations of all ions studied, except Zn, were higher in throughfall and stemflow than in precipitation ($p < 0.01$). The dominant elements in throughfall and stemflow were S, Ca and Mg. Nickel concentrations were higher in rainfall and throughfall relative to drainage water and stemflow, respectively. Throughfall from plants amended with litter contained more K (3.0 mg L^{-1}) and Ni (1.3

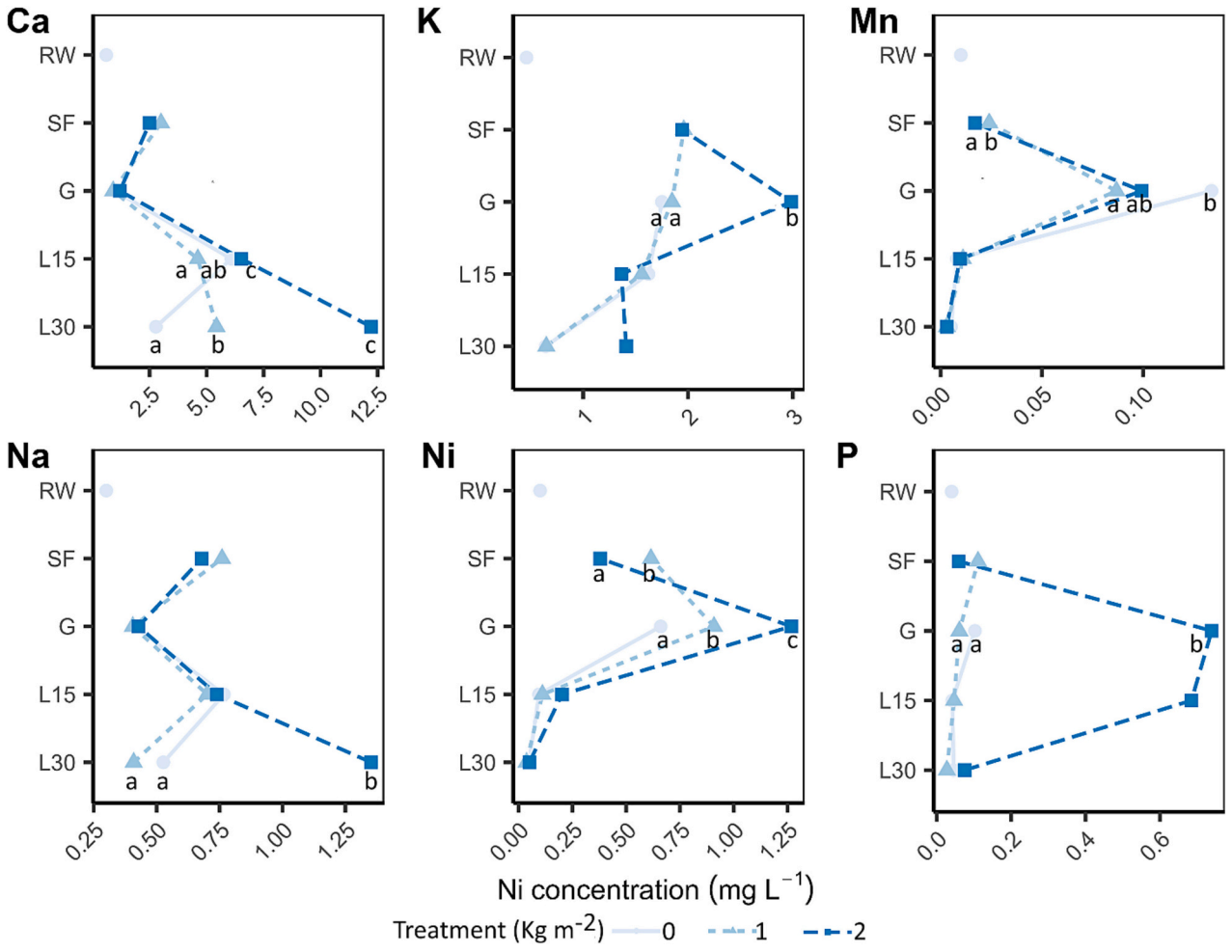

Fig. 2. Element concentrations of water of the different litter treatments in mg kg^{-1}. Differences between treatments are indicated with lowercase letters ($p < 0.05$) RW: Rainwater ($n = 15$); SF: Stemflow ($n = 45$); G: Throughfall (n = 45); L15: Gravity water 15 cm (n = 15); L30: Gravity water 30 cm (n = 15).

mg L^{-1}) than plants non-amended with litter ($p < 0.01$). On the contrary, throughfall of control plants was more concentrated in Mn (0.13 mg L^{-1}; p 0.4). Stemflow of 2 kg m^{-2} litter treated plants was less concentrated in Ni (0.4 mg L^{-1}) and Mn (0.02 mg L^{-1}) compared to the 1 kg m^{-2} litter treated plants (p 0.03). No other effect of treatments was visible on stemflow concentrations.

The amount of precipitation, throughfall, stemflow and gravity water varied strongly with time. Driest season period was in February–March and wettest period was in December–January (Fig. S4). Nickel concentrations in water varied with time from <0.05 mg L^{-1} at the beginning of the experiment to >10.4 mg L^{-1} in March 2019 (Fig. 3). Nickel concentrations in drainage water were always lower than stemflow and throughfall. Nevertheless, Ni concentrations in gravity water tended to be higher at 15 cm depth for the high dose litter treatment (p 0.11) (Fig. 4). Ni concentrations in the stemflow and throughfall were low and increased at the end of 2018. (Fig. S4). Tendencies of higher litter treatment to release more Ni in water was measured; Ni in throughfall was higher in the 2 kg m^{-2} and occasionally higher in the 1 kg m^{-2} treatment, notably in March 2019 compared to control ($p < 0.01$). Nickel quantities released from throughfall were two times higher for high dose treatment (2.2 g m^{-2} y^{-1}) than non-treated plants (1.1 g m^{-2} y^{-1}) (Fig. 4). Throughfall was a major input flux for Mn, Ca, K, Mg, Na, P and S (Table 3). Stemflow had a relatively low effect on elements input compared to throughfall. Nevertheless, throughfall was overestimated because plant leaves did not cover all the soil surface.

3.4. Litterfall fluxes in the system

Litter fluxes varied with time from July 2018 to January 2020 (Fig. 3). Nickel concentrations were lower in June 2018 at the beginning of the experiment in litterfall and varied from 5000 mg kg^{-1} (0.5 wt%) to 53,000 mg kg^{-1} (5.3 wt%). Litterfall was less concentrated in Ni when plants were amended with litter ($p < 0.01$). The quantity of Ni from litterfall was lower at the beginning of the experiment since plants had lower biomass stand; Ni quantity varied and increased until 18 g m^{-2} at the end of 2019. Litterfall flux was the major input flux in soils for Ni and Zn. An input of 3.1 g m^{-2} y^{-1} of Ni by litter for non-treated plants was recorded in 2019. Litter flux was significantly lower for treated plants, about twice less (1.5–1.6 g m^{-2} y^{-1}; p 0.3) (Fig. 4). Calcium input by litter (0.5 g m^{-2} y^{-1}) was five times lower than Ni input by litter (Table 3).

3.5. Litter decomposition in the system

Litter bags degradation reflected degradation of the litter treatments of all the plots studied at the moment of collection (Fig. 5, Table S9). The decomposition constant, k was 0.8 on average but varied with time and organs considered ($p < 0.01$). Leaflet degradation was faster (k = 1.1) than wood (k = 0.3) and petiole degradation (k = 0.8). More than 450 days after the first litter treatments application, 68 % of the litter was still remaining in bags. Degradation varied as a function of the element

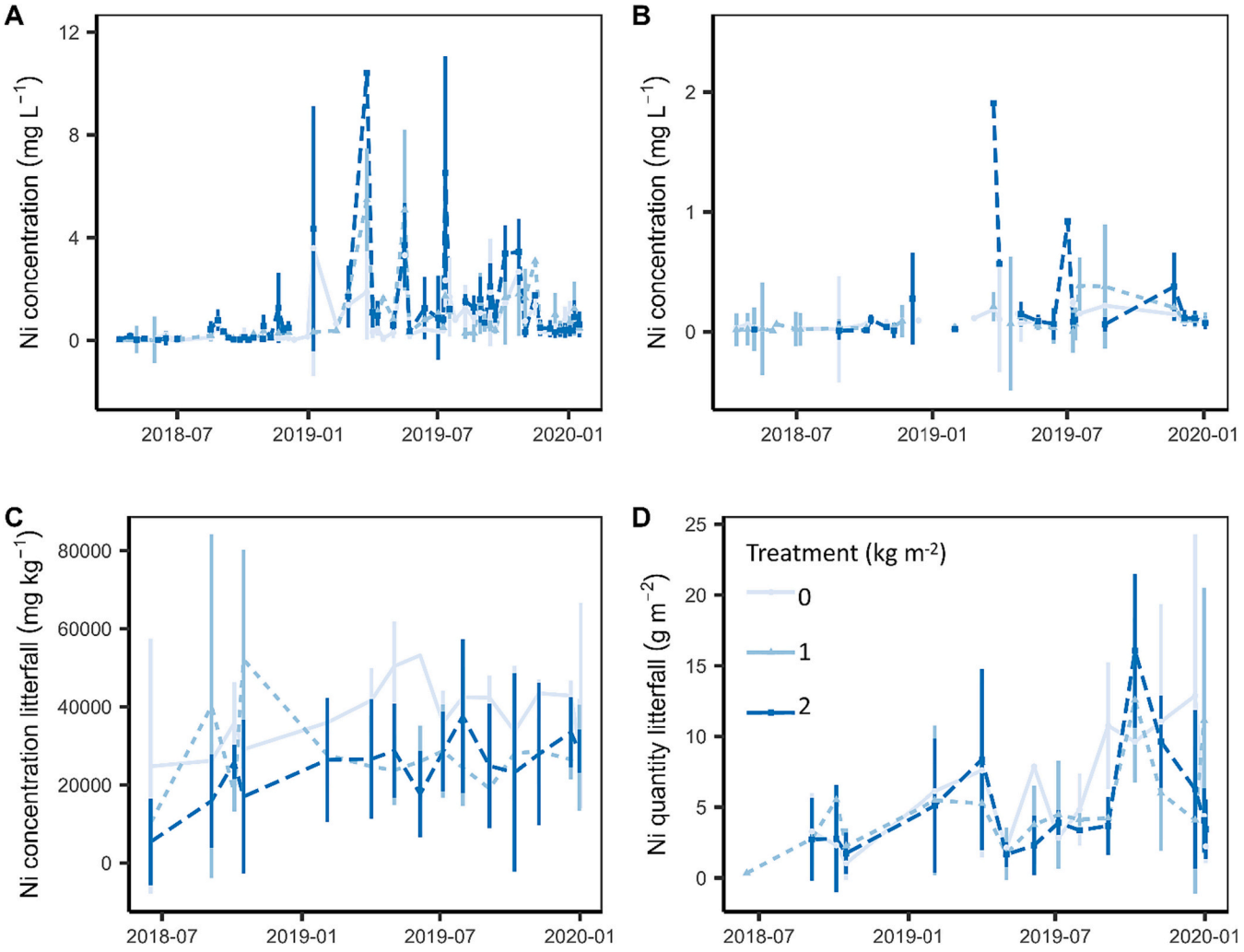

Fig. 3. Nickel concentration and quantity of Ni fluxes over time (means ± standard deviation; n = 3). A: Ni concentration of throughfall in mg L^{-1}; B: Ni concentration of stemflow in mg L^{-1}; C: Ni concentration of litterfall in mg kg^{-1}; D: Ni quantity from litterfall in g m^{-2}.

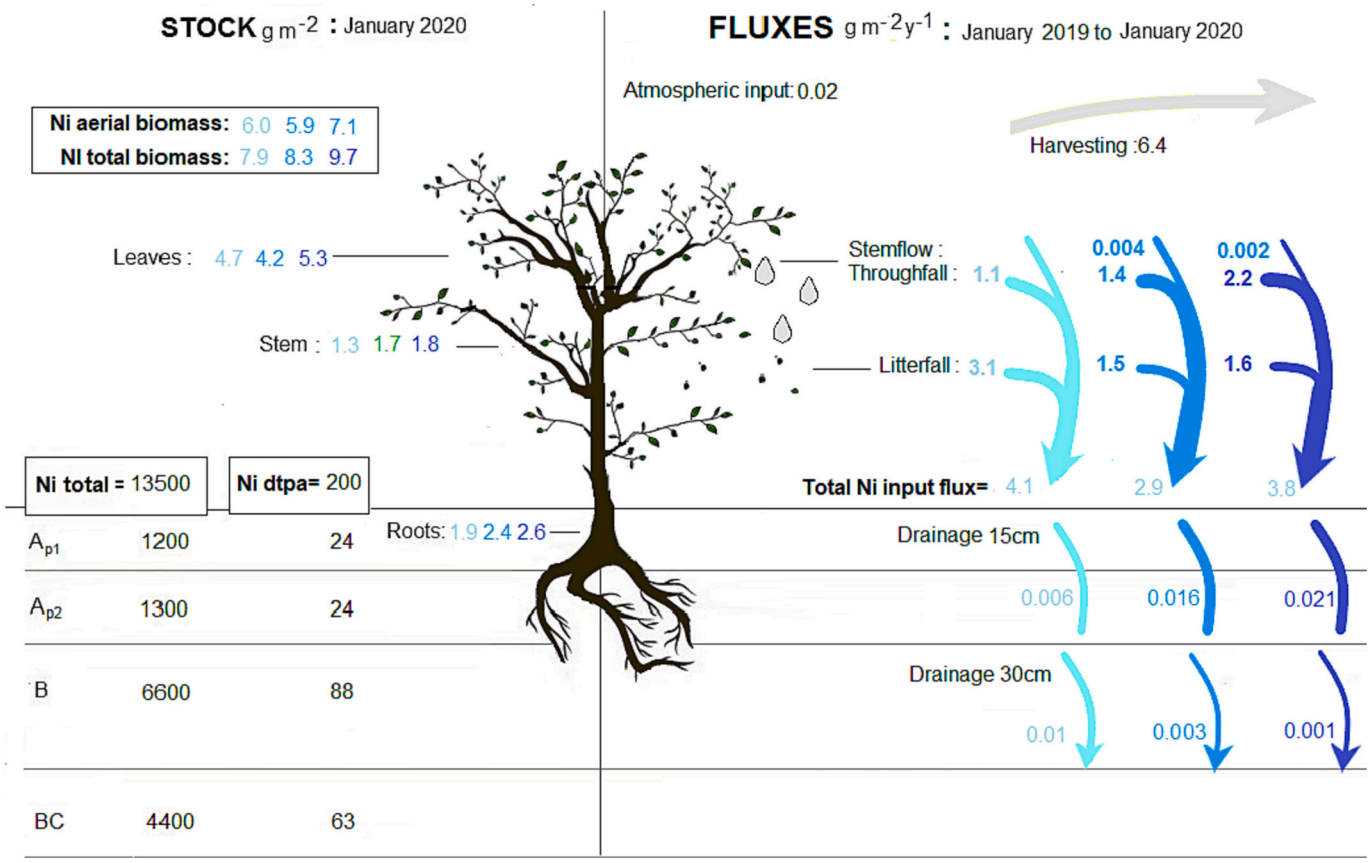

Fig. 4. Nickel biogeochemical cycle of a Phyllanthus rufuschaneyi of the first tropical metal farm from January 2019 to January 2020. Stocks in g m^{-2} and fluxes in g m^{-2} y^{-1}. Litter treatment: Light blue 0 kg m^2 Blue 1 kg m^2; Dark blue 2 kg m^2.

studied. Litter decomposition rate did not indicate Ni release from litter. During the first three months, Ni concentrations in leaflets and wood did not vary (2.2 wt% and 0.6 wt%). Nickel concentrations in leaflets increased to 3.8 wt% after 4.5 months. Nickel concentration in leaflets was still 3.0 wt% eight months after the first litter input. Nickel concentrations in petioles did not statistically vary with time (1.3 wt%). Fifteen months after treatment application, Ni concentrations in all the plant fractions were similar (1.0 wt%). The release of K from litter was the fastest relative to all elements and was completely leached out after only four-months (Table S9). Other elements such as Ca and S were not significantly leached out after 15 months.

3.6. Annual elemental budget of the system

Annual soil element budget was calculated with flux from January 2019 to January 2020 (Table 2, Fig. 4). This annual budget is positive for K, Na, P and S but negative for Ca, Mn, Ni and Zn. It is important to note that K and P budget are positive only due to the fertilisation applied in November 2018 and would be negative without it. The primary nutrient return was highest for S (64 g m^{-2} y^{-1}), followed by Ni (4.2 g m^{-2} y^{-1}) and Ca (2.6 g m^{-2} y^{-1}). Biomass harvesting was the main output for all the elements, except for S that was preferentially lixiviated (4.1 g m^{-2} y^{-1}). Nickel leaching was very low (0.01 g m^{-2} y^{-1}), even lower than atmospheric deposition (0.02 g m^{-2} y^{-1}). Nevertheless, Ni in gravity water was higher at 15 cm than at 30 cm, indicating that a part of the Ni leached in the surface horizon was reabsorbed within the B horizon. The Ni cycle was mainly driven by litterfall (3.1 g m^{-2} y^{-1}) and biomass export (6.4 g m^{-2} y^{-1} for two plants per m^{-2}). No statistical difference was visible between the annual nutrient budget of treated soils and the control soil.

3.7. Biochemical sub-cycle of the system

Only Mg accumulated preferentially in the roots, in contrast to all the other elements (Table 4). Translocation factors were influenced by litter for Mn and Mg (Table 4). Nickel translocation factor was 1.9. Leaves from plants amended and non-amended with litter had the same Ni (20,000 mg kg^{-1}) and Zn (190 mg kg^{-1}) concentrations. The same pattern was measured in the litterfall of these plants. Litterfall of control plants was more concentrated in Mn (420 mg kg^{-1}) and Mg (300 mg kg^{-1}) than litterfall of plants treated with litter. The latter was more concentrated in Ca (9800 mg kg^{-1}) and P (450 mg kg^{-1}) relative to the control. Concentrations between leaves and litter are different for numerous elements. Senescent leaves contained more Ni, up to 37 % and 86 % of the total Ni concentrations in whole plant in the treated and control plants, respectively. Calcium, Mn, and Zn were also more concentrated in senescent leaves, whilst K, Mg, P and S were reabsorbed. Approximately 70 %, 50 % and 30 % of P, S and K were respectively reabsorbed by *P. rufuschaneyi*.

4. Discussion

4.1. Balance and fluxes of nickel in the system

Nickel concentration and availability in ultramafic soils vary as a function of soil chemical and mineralogical parameters (Echevarria, 2021). In this study, Ni is principally stored in the BC horizon (6400–8700 mg kg^{-1}) of the plot, indicative of the substantial Ni concentrations in the subsoil and a relative depletion of total, and sometimes available, in the surface horizons, probably as a consequence of intense Ni lixiviation. The available Ni concentrations do not vary significantly along the soil profile; (Table 1). On the contrary, the nearby

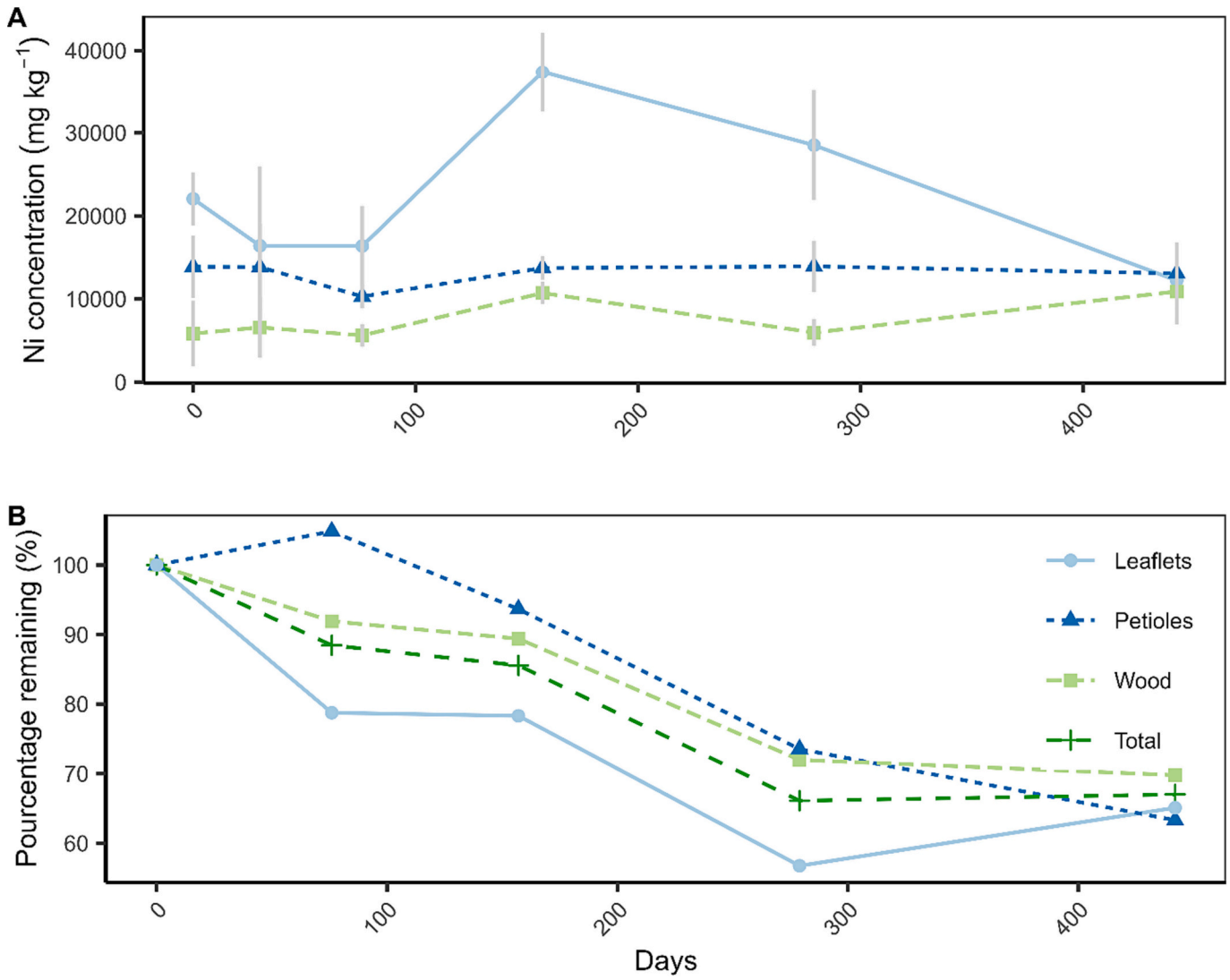

Fig. 5. Litter bags biomass and Ni concentration in function f time from middle 11/2018 to end 01/2020 of the different component of the litter bags. A: Ni concentration of litterbags in mg kg^{-1}; B: Litter remaining in percentage (n = 3).

Table 4
Elemental concentrations in leaves and litter in kg m-2, their differences in % and translocation factor (TF). Only means followed by letter are significantly different ($p < 0.05$ level) (n = 3).

	Litter kg m^{-2}	Mn	Ni	Zn	Ca	K	Mg	P	S
Litter (mg kg^{-1})	0	420 a	38,000 a	320 a	8000 b	4400	3000 a	270 b	1200
	2	270 b	26,000 b	213 b	9800 a	5100	1900 b	450 a	1200
Differences (%)	0	91	86	77	45	−33	−3	−71	−48
	2	23	37	42	53	−30	−34	−54	−50
TF	0	1.8	1.9	1.5	1.1	1.2	0.9	1.3	1.6
	2	1	1.8	1.3	1.1	1.3	0.6	1.5	1.7

topsoil (5 km) of a typical Ni hyperaccumulator plants dominated forest (Garras; Lompoyou Hill) is enriched in available Ni relative to the subsoil due to substantial Ni enriched leaf litter recycling (Tisserand et al., 2022). The relatively high available Ni concentrations in the soil is indicative of the clayey nature of the ultramafic soil, or at least of its B horizon (Fig. S2), with high exchange capacity for Ni: Nickel extractability is relatively high in clayey ultramafic soils as well as soils dominated by amorphous Fe-oxides bearing phases compared to highly crystalline Fe-oxides (Echevarria, 2021; Massoura et al., 2006; Raous et al., 2010; van der Ent et al., 2018a, 2018b). Notably, the non-available Ni stock is also high and could potentially replenish the labile Ni pool, possibly by mineral weathering, but this is a relatively slow process which depends on the local buffering system (Massoura et al., 2004; Vithanage et al., 2019). In two years of agromining, the total Ni concentrations increased in our study in the upper horizon, even without litter treatment. Besides direct contribution from decaying nickel-rich plant material (e.g. roots), plant cultivation could indirectly affect Ni release (Risse et al., 2024) from weathering rocks due to roots uptake and exudation. Nickel concentration in roots is significantly higher than DTPA-Ni in surrounding soil, suggesting strong Ni uptake mechanisms. Nickel hyperaccumulator plants have been reported to take up Ni from the same labile soil pool as non-hyperaccumulator

plants, but at much higher rates (i.e. 100 times more) than the latter (Massoura et al., 2004).

Total litter degradation has a constant degradation of 0.8 over a year on average. The degradation of herbaceous hyperaccumulator plants could be relatively faster with a rapid release of Ni (Boyd et al., 2008; Echevarria, 2021). This degradation can be compared to the litter degradation on non-ultramafic soil in Malaysia (Anderson et al., 1983). In tropical climates, rapid litter degradation is expected due to high temperature and rainfall and a study in the same region of Malaysia found a constant degradation similar to temperate forest (Sellan et al., 2022). The woody parts of tropical hyperaccumulator plants can slow the degradation process, as observed in this study. Nickel leached out from the litter increases the soil Ni available pool (Tisserand et al., 2021); Ni available stock was doubled in 15 months. However, the extent of availability of the Ni fraction is influenced by the prevailing local Ni bearing phases. Leached Ni from litter increases with amount of litter deposited and tends to be higher in the A horizon relative to B horizon. Notably, the B horizon tends to be more concentrated in clays that can store exchangeable Ni and increase its stock from which roots can access at least down to 40 cm. Very limited Ni lixiviation was measured in this study, probably due to the presence of this B horizon. A study on Ni transfer from soil to water was conducted in the same area and is consistent with our results (Tashakor et al., 2017) and would tend to downplay the role of hyperaccumulator vegetation in retaining Ni in the topsoil from lixiviating. Indeed, low concentrations of Ni were found in surface waters flowing over the ultramafic massifs, only 14 g L^{-1}. Agromining in a tropical, non-saturated-water environment would therefore not increase the transfer of Ni to the environment (e.g. groundwater).

This study reveals that there was no significant increase in foliar Ni concentrations of *P. rufuschaneyi* when the soil had much higher available Ni, suggesting DTPA-extractable Ni concentrations are not limiting in Pahu soils for this species. The Ni stocks in the plant biomass was mainly localised in both old and young leaves; concentrations in roots increased with increasing amount of litter but the Ni stock in aerial biomass did not. Although litter treatment did not increase Ni concentrations in living leaves, it increased Ni concentrations and quantities in throughfall. These observations could be due to an equilibrium between Ni intake in leaves and Ni losses through leaf leaching. Increase of Ni in throughfall could be also due to the higher amount of aerial biomass. Litter from amended plants are 50 % more concentrated in Ni than fresh leaves and 86 % more concentrated in Ni than litterfall from non-amended plants. No Ni depletion in plant organs of non-amended plants was visible, so we considered that this increase came from a higher Ni return flux to balance the removal of Ni by the roots. A lower Ni return to soil was observed for litter treated plants, probably because Ni available pool was already higher in surface soil with no need of the plant to recycle Ni intensively.

4.2. Balance and fluxes of major nutrients in the system

Ultramafic soils have relatively low concentrations of P, S, K and Ca compared to non-ultramafic soils (van der Ent et al., 2016). Local hyperaccumulator plants accumulate substantial concentrations of these essential nutrients in foliar tissues on ultramafic soils despite their relatively small stocks in ultramafic soils (van der Ent and Mulligan, 2015). These elements are reabsorbed by the leaves before senescence, especially P. Potassium, however, leaches readily and correlates positively with leaf degradation (R^2 0.92; p 0.03), compared to Ca. Under high litter stock, plants tend to return less elements to the soil, except for Ca and P. Decrease in P stock due to harvesting can lead to a limitation of this nutrient; P is often limited in tropical forests (Vitousek, 1984). A limited P fertilisation has to be carried out to avoid a decrease of biomass production under agromining, but that takes into account that high levels of P and especially K inhibit the growth of *P. rufuschaneyi* (Nkrumah et al., 2019b; Tisserand et al., 2021). The Ca budget is negative whereas Ca amendment has a positive effect on the Ni yield of *P. rufuschaneyi* (Nkrumah et al., 2019c); and hence, it is likely that depletion decreases Ni agromining yield in the long term. However, the increase of concentrations of K and Ca in aerial biomass is not desirable because ashes need to be washed to remove these elements, moreover, excess K leads to slower growth of *P. rufuschaneyi*. The K budget is negative if only litterfall input is considered. Strong K addition decreased Ni yield in pots (Nkrumah et al., 2019b, 2019c). If the depletion of K was to continue at the same rate, K fertilisation would be needed at a moderate rate, to avoid negative impacts on plant growth. Soils under both litter treatments are more concentrated in K. Also litter treatment increased exchangeable Na, P, S and K and the corresponding total concentrations. This effect was not shown on total soil concentration amended with *O. chalcidica* litter (Echevarria, 2021) and suggests that occasional litter treatment could probably compensate the nutrient losses due to the high capacity of litter to supply these elements under available forms to the topsoil. Litter input modifies translocation factors of Mg and Mn; when litter is present, these factors are reduced due to an increase of their concentrations in roots. Less Mn returns to the soil by stemflow and less Mg and Mn return by litter input are observed. Litter deposit results in a lower translocation of Mn and Mg to aerial biomass and a lower return of this element back to the soil.

4.3. Biogeochemical role of hyperaccumulator plants in the system

As emphasized in several studies, Ni hyperaccumulator plants are believed to play a significant role as pioneer species in strongly enhancing nutrient fertility in topsoils because they release large amounts of K and Ca to topsoils through litterfall (Echevarria, 2021). As expected from the allelopathy hypothesis (Boyd et al., 2008), a strong and rapid enrichment in available Ni might also favour faster colonisations of the species in recently cleared ultramafic areas. Significant coverage of the soil by *P. rufuschaneyi* results in a rapid increase in Ni availability but also in a strong enrichment of essential nutrients such as K, P and Ca (Tisserand et al., 2022), thus increasing strongly nutrient fertility for other plants. *Phyllanthus rufuschaneyi* can also be considered a pioneer plant due to its extraordinary capacities of this hyperaccumulator to build up chemical fertility in soils in a very short time. Because K availability and soil organic matter will increase with time, they will negatively affect *P. rufuschaneyi,* the species will slowly disappear and leave room to other Ni hyperaccumulators (Nkrumah et al., 2019d) that are more adapted to more shade and close forest conditions such as *Rinorea* cf. *bengalensis*. This increase in P and K could also promote non-hyperaccumulators plants, as *Dryobalanops lanceolata* whose occurrence is limited by theses nutrients in this region (Brearley, 2005).

4.4. Implications for nickel agromining and conclusions

The number of harvests that will results in a to significant depletion of the initial labile Ni pools is still unknown and unpredictable after two years of experiments. Agromining operations harvest Ni-rich shoot biomass, which will limit Ni recycling through leaf litter. Even under sustained agromining, litterfall is significant. After almost two years of cropping, no decrease of Ni available pool has been recorded. Nickel litter fluxes combined with weathering could be sufficient to replenish Ni available pools under agromining employing *P. rufuschaneyi*. Biomass harvesting depletes essential and trace nutrients. Therefore, moderate fertilisation, especially P, would be required to avoid complete nutrient depletion in a sustainable Ni agromining, but moderate and occasional litter amendment might be sufficient to compensate for these losses. This study highlights the biogeochemical cycling of Ni and physiologically relevant elements in a tropical agromining metal farm. The Ni cycle of tropical hyperaccumulator plants is mainly driven by internal cycles. Nickel is returned to soil by litterfall even under sustained harvesting. After two years, no decrease of Ni pool was noticed. Tropical Ni

agromining could be economically viable for many years, however the exact timeframe is yet to be determined. Indeed, large-scale demonstrations of tropical agromining profitability are needed, such currently as in Brazil (Nascimento et al., 2022).

From all the data generated in this study, it is obvious that Ni is released through mineral weathering which is a key parameter to understand the stability of Ni availability over time when no litter is returned. The estimation of such a release on Ni budget in the system is crucial to understand the full cycle of this element in such ecosystems. For this purpose, Ni stable isotope fractionation approaches be used to further clarify the processes involved in the Ni biogeochemical cycling in a wet tropical hyperaccumulator plant environment. From an applied perspective, weathering and root uptake studies could also predict the effect of Ni input and output flux on available Ni pool and thereby estimate the potential time scale of tropical Ni agromining.

CRediT authorship contribution statement

Romane Tisserand: Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Software, Validation, Visualization, Writing – original draft, Writing – review & editing. **Antony van der Ent:** Conceptualization, Methodology, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. **Philip Nti Nkrumah:** Visualization, Writing – original draft. **Serge Didier:** Conceptualization, Investigation, Methodology. **Sukaibin Sumail:** Investigation, Methodology. **Jean-Louis Morel:** Conceptualization, Investigation, Supervision. **Guillaume Echevarria:** Conceptualization, Data curation, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Validation, Visualization, Writing – original draft.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.170691.

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