Landscape cultivation alters $\delta^{30}$Si signature in terrestrial ecosystems

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Despite increasing recognition of the relevance of biological cycling for Si cycling in ecosystems and for Si export from soils to fluvial systems, effects of human cultivation on the Si cycle are still relatively understudied. Here we examined stable Si isotope ($\delta^{30}$Si) signatures in soil water samples across a temperate land use gradient. We show that – independent of geological and climatological variation – there is a depletion in light isotopes in soil water of intensive croplands and managed grasslands relative to native forests. Furthermore, our data suggest a divergence in $\delta^{30}$Si signatures along the land use change gradient, highlighting the imprint of vegetation cover, human cultivation and intensity of disturbance on $\delta^{30}$Si patterns, on top of more conventionally acknowledged drivers (i.e. mineralogy and climate).

Dissolved silicate (DSi), as released from chemical weathering of silicate minerals, is involved in numerous biogeochemical reactions prior to its discharge in rivers12. Continental vegetation mediates weathering rates, in particular in soil micro-environments influenced by roots13,4. Yet plants can also take up considerable amounts of DSi from soil water5,6 which can be recycled in the soil from falling litter and dissolution of the amorphous biogenic Si structures (BSi) or phytoliths in plant’ tissues2,7. Biogenic Si production in terrestrial forests23 or grassland24. Here, we aim to isolate the role of land use change by examining the Si isotopic variation of soil water. Currently only a limited amount of DSi is at least an order of magnitude larger than the annual export of dissolved and biogenic Si towards the coastal zone9,10 and is thus too large to be solely derived from newly mobilised Si11. The soil-plant system can be seen as an ecosystem filter4 buffering the actual release of Si to rivers by recycling of reactive amorphous Si in ecosystems (soils + plants). Human activities have perturbed this terrestrial Si filter, with effects persisting in rivers, estuaries and coastal zones8,10,12–14. Prolonged landscape cultivation and intense agricultural expansion have lowered DSi fluxes to rivers8,15 and diminished soil amorphous (i.e. both biogenic and non-biogenic) Si stocks due to agricultural Si harvest16–18 or due to Si losses after surface erosion12. Although crop removal can rapidly (i.e. ~10 years) induce top soil depletion of phytoliths19, timescales at which human cultivation impacts on soil Si dynamics and export from soils towards fluvial systems are not well understood11. Mechanisms controlling Si cycling in the soil-plant system are likely separated in time, from relatively quick adsorption/desorption reactions (seconds), to neoformation and dissolution of clay minerals (10–1000 years or more)19 via the intermediate residence time of biogenic Si. Moreover, changes in clay mineralogy may be amplified by vegetation cover20,21 and management practices in cultivated soils (e.g. fertiliser use)22.

Stable Si isotopes have been successfully applied to define Si sources and sinks along the ecosystem flow path2,21,23–27. Intense fractionation of Si isotopes occurs during chemical weathering27 and rivers are generally enriched in $\delta^{30}$Si isotopes ($\delta^{30}$Si of $\sim -0.10\%$) compared to the source bedrock27,29 ($\delta^{30}$Si of bulk upper continental crust is $\sim -0.25\%$). Several mechanisms may cause this enrichment: clay neoformation21,29,31, Si adsorption onto Fe and Al oxides32,33 and Si uptake in plants26,27,34. It has been recently suggested that the light Si isotopic composition of clays formed during weathering is inherited from early fractionation during Si adsorption onto amorphous Al-hydroxides35. Dissolution of secondary clay minerals can therefore enrich solutions in the light isotopes. Stable Si isotopes are currently underexploited in the end-product of the soil-plant system: the soil water. Currently only a limited amount of DSi $\delta^{30}$Si data in soil water is available and research is predominantly focused on variation within one weathering profile or within one natural ecosystem or land use type, such as forest23 or grassland41. Here, we aim to isolate the role of land use change by examining the Si isotopic variation of soil water DSi in different ecosystems characteristic of Western European landscapes: i) a deciduous oak/beach forest, ii) a cultivated grassland (pasture), and iii) two croplands with row crops differing in duration of
cultivation (cropland with short (~30 years) and long (at least 240 years) duration of cultivation is called “young” and “old” cropland throughout this work). The land use change gradient is perfectly fitted to meet our objectives, as we can rely on similar bulk mineralogical and climatological properties and a considerable number (n = 102) of soil water DSI δ³⁰Si samples. Clay mineralogical differences between sites can be fully related to land-use effects. Supplementary tables S1–S6 provide further details on the land use gradient (soil characteristics, bulk and clay mineralogy,...).

Results and Discussion

A clear δ³⁰Si signature. Si isotopes were analysed on a selection of soil water DSI samples from a long-term operative sampling network (Fig. 1; Supplementary Table S7 for raw δ³⁰Si, δ²⁹Si and DSI data). Selection covers within-site variability, including soil depth, topographical gradients and distances along the slope perpendicular to the draining river (Supplementary Fig. S1). The highest and most stable mean soil water DSI δ³⁰Si signatures are found in the old cropland (δ³⁰Si = +1.61 ± 0.12), intermediate in pasture (δ³⁰Si = +1.05 ± 0.21) and young cropland (δ³⁰Si = +0.89 ± 0.31) while the lowest δ³⁰Si and most variable signatures derive from DSI in forest soil water (δ³⁰Si = +0.62 ± 0.34) (Fig. 1). Average soil water DSI δ³⁰Si signature differences between sites are significant (p < 0.05) for forest vs. pasture, forest vs. old and vs. young cropland, old vs. young cropland and pasture vs. old cropland but not for young cropland vs. pasture. Within-site variation in DSI δ³⁰Si was only significant for pasture (Supplementary Table S8–9).

Explaining δ³⁰Si variation along the land use change gradient. Plant-soil cycle. Soil BSi storage is strongly effected by land use changes (Fig. 2a). Biological Si recycling in the root zone has been shown to control DSI concentrations in soil and export water and could partly control its δ³⁰Si, due to the discrimination against heavier isotopes of Si during plant uptake26–27,34. In forests, intense Si cycling occurs in the plant-soil system2 (and references therein), with annual Si uptake into biomass equal to or larger than annual Si return to soil as litter fall, and thus a strong turnover and potentially large storage in BSi reservoirs. Given the rapid decline of BSi concentrations down the soil profile (i.e. from ~8 and <0.1 mg BSi/g at 5 and 40 cm respectively; Fig. 2a), long-term BSi burial in the forest soil can be omitted in this study. Light isotopes from litter are thus released into soil solution, especially during the replenishing of soil water during and after rain events35, which occur year-round in the study area. (Semi)-natural grasslands, as well as forests, show tight Si cycling in vegetation and soil24,36. Some studies relate stable BSi pools of grasslands to more resistant grass phytoliths37. As grass species in general are the worlds’ largest Si accumulators6 and have higher BSi contents compared to forest litter (i.e. in this study an average of 0.9% BSi in grass versus 0.6% BSi in forest litter), they could also have a higher potential for DSI uptake and therefore a stronger impact on soil water δ³⁰Si signatures during growth. Mowing and grazing in pastures and croplands reduces the return of DSI to soil water associated with litter-decomposition, likely resulting in a generally higher DSI δ³⁰Si signature relative to forest. At the surface efficient harvest in croplands could explain the depletion of soil BSI (Fig. 2a) and higher DSI δ³⁰Si signature (Fig. 1). While the young cropland soil water DSI δ³⁰Si is still impacted by a pool of persistent soil phytoliths enriched in δ²⁹Si, BSi dissolution (and associated release of δ²⁹Si) is of minor importance in the old cropland. Moreover, higher DSI uptake by

Figure 1 | Bar charts of soil water DSI δ³⁰Si in different sites. From top to bottom: (a) deciduous forest (Ronquières), (b) pasture (Blémy), (c) young cropland (Ganspoel) and (d) old cropland (Velm). Data are categorised in 19 size categories of δ³⁰Si, ranging from −0.1 to 1.8‰. The dark part of the bar shows the samples in the unsaturated soil, the grey parts of bars show the samples collected in the saturated soil. See supplementary information for more details on δ³⁰Si values and sampling selection.
wheat as compared to corn (in young cropland), and thus higher plant BSi content (average of 1.3% versus 0.3% BSi respectively; Supplementary Table S10) may further deplete soil in the perennial arable field, and enrich soil water with $^{30}$Si.

Weathering. Despite homogeneous climate and bulk mineralogy, clay evolution and weathering regime can be altered by land use. Different Si isotope fractionations caused by clay differences could partly control soil water DSI $^{30}$Si signatures. We have indications that our forest site is more prone to chemical weathering and clay dissolution$^{23,38}$, driven by lower pH minima and higher production of organic matter. Lower values for total reserve in bases (TRB; lower TRB indicates a higher degree of soil weathering) are calculated in our forest site, which may emphasise the importance of small scale variation (as also reflected by the large range in DSI $^{30}$Si in soil water). Saturation indices in soil water show further dissolution of secondary precipitates as an important process in all land uses (Supplementary Table S11). It could be argued that higher forest heterogeneity facilitates conditions for consecutive clay dissolution and precipitation processes (i.e. as shown by smectite precipitation in forests in some cases). However, without clear insight into Si isotope fractionation patterns in (2 : 1) clays, impact of clay evolution on soil water DSI $^{30}$Si remains unquantified.

Other factors. Apart from Si fractionation due to plant-soil cycling of Si and weathering processes, the addition of light Si isotopes to the soil solution can be altered by other factors, such as the ratio and occurrence of adsorption/desorption processes, the use of fertiliser and impact of local hydrology. Si fractionation occurs during DSI adsorption and although quite small initially (i.e. 0.5‰) fractionations can range up to about 3‰ due to successive dissolution/precipitation and adsorption/desorption processes$^{27}$. Low amounts of adsorbed oxalate-extractable Si are present in our soils (i.e. range of 0.03–0.42 mg Si$_{ox}$/g) and large differences in Si$_{ox}$ between study sites are absent (Supplementary Table S5). A large impact on Si isotope fractionation driven by adsorption/desorption processes can thus probably be ruled out here. Furthermore, hydrological variations and in particular the position of the groundwater table is likely influencing soil water DSI $^{30}$Si signatures. When $^{30}$Si signatures of the unsaturated and saturated zone in pasture and forest systems are plotted separately (Fig. 1, respectively black and grey bars), differences between land use DSI $^{30}$Si become more prominent (note: for cropland soil water $^{30}$Si there is no effect of hydrology as all soil water samples from croplands in this study are collected from the unsaturated zone). More specifically, the mean stable Si isotopic signature of soil water DSI varies within the pasture system and along the slope perpendicular to the river: highest DSI $^{30}$Si values are measured in soil water sampled from the unsaturated zone at the plateau ($^{30}$Si = $+1.27 \pm 0.20$) and lowest values in soil water from the saturated zone in the valley ($^{30}$Si = $+0.91 \pm 0.11$) (Supplementary Table S7 and Fig. S1). Finally, organic fertilisers (i.e. derived from plant remains and/or manure) applied to the croplands are unlikely to be responsible for DSI $^{30}$Si differences along the land use change gradient, as BSI input through fertilisers (i.e. $\sim 10$ kg of BSI ha$^{-1}$; Supplementary Table S10) only corresponds to circa 10% of the annual BSI export due to crop harvest (112–127 kg BSI ha$^{-1}$ year$^{-1}$). More importantly, there is a lack of correlation between the Si isotopic composition and the fertiliser-derived elements (such as Mg and K) in the soil water of the old cropland. We therefore expect that increasing export of light $^{28}$Si isotopes in cultivated land uses, and higher recycling of $^{30}$Si and elevated weathering intensity (including clay dissolution) in forest systems will largely determine soil water DSI $^{30}$Si signatures of our systems (Fig. 3). Our data do not allow to distinguish biological from pedogenic processes, but point to the interaction of both. At a catchment scale, this still results in an altered Si isotope signature in most soil solutions.

Conclusions and implications. Our results imply that soil water DSI $^{30}$Si signatures are modified through soil management before reaching rivers and coastal zones, where other fractionation processes may take over (e.g. diatom uptake or reverse weathering in floodplains). The imprint of land cover and its related biological and pedogenic processes is potentially high: the soil water $^{30}$Si range ($-0.11$ to $+1.81$‰) in this homogeneous small scale study only impacted by a changing land use and duration of cultivation covers almost 50% of observed global riverine DSI $^{30}$Si variation (see Supplementary Fig. S2 for an overview of river, soil and groundwater DSI $^{30}$Si). As human cultivation can put constraints on the DSI $^{30}$Si soil water signal of distinct land use systems, the signal - or parts of it - can potentially be transferred to the DSI $^{30}$Si signature of adjacent fluvial systems. Indeed, our DSI $^{30}$Si soil water signal matches well with DSI $^{30}$Si variation in rivers draining
neighboring catchments in Belgium (0.46–2.09%), which was unrelated to diatom growth, yet could be correlated to distinct vegetation covers: forest and arable land with row crops resulted in average low $\delta^{30}\text{Si}$ values in river water respectively. Our results allow a more direct link between land cover and soil and river water DSi $\delta^{30}\text{Si}$ signatures. Future research needs to better constrain the magnitude of processes associated with Si fractionation during land cultivation. No geographical counterparts of land use change gradients currently exist, and validation of our results in other systems worldwide is essential.

A transient $^{28}\text{Si}$ sink? Mounting evidence challenges the steady-state of the contemporary Si cycle (i.e. at human time scales of less than 1000 years), as land use conversions alter or even hinder Si recycling and introduce transient non-steady state conditions of Si in terrestrial ecosystems. Global annual agricultural Si harvest is estimated around 8 Teramole Si, a value which is comparable with the amount of dissolved silicate transported in rivers worldwide. As at least part of the harvested Si is likely not recycled back to the soil-plant system and ends up in transient to permanent sinks (e.g. construction materials, sludge,...), this...
implicitly involves removal of $^{30}\text{Si}$ from cultivated systems. Our data strengthen the hypothesis that long-term intensive cultivation is lowering DSI export towards semi-closed coastal environments (estuaries and within restricted seas like the North Sea), yet the exact change in $\delta^{30}\text{Si}$ signal reaching rivers remains currently unquantified. Land use change effects on soil and river DSI and thus $\delta^{30}\text{Si}$ will probably become more pronounced in systems where biological cycling, uptake and fractionation of Si is very high. For example, annual uptake of dissolved Si by rice growth alone is five times higher than the Si flux in the Yangtze River$^{25,26}$ and Si sequestration in rice is at least one order of magnitude higher than concentrations of plant BSi observed in this study. Furthermore, steady state of the global biogeochemical Si cycle on longer than human timescales (>1000 years) is no longer self-evident, as lakes and reservoirs for example are likely accumulating reactive Si (including BSi) enriched with light Si isotopes$^{11}$. Apart from having implications for estimations of weathering rates, a change in the efficiency of Si retention in lakes and reservoirs suggests that the flux and isotopic Si composition of dissolved Si reaching the ocean has varied correspondingly. As rivers supply about 85% of the annual DSI input to the surface ocean, and are the main source of Si for the ocean balancing annual export of BSI to the ocean sediments, the potential impact of a change in $\delta^{30}\text{Si}$ from continents to river on historical and contemporary productivity estimates in closed basins and coastal zones deserves better attention, as it is often assumed that the Si isotopic composition of river DSI has remained constant in time$^{11}$. Our results demonstrate that both $\delta^{30}\text{Si}$ is a useful and sensitive indicator to identify and quantify impacts of human cultivation and soil disturbance on the terrestrial Si cycle, with the potential to track subtle changes in clay evolution and biogenic sink/source functions induced by land use change.

### Methods

#### Study site description

The land use gradient is located in the loess belt of Central Belgium, where climate is temperate, without a dry season and with a warm summer (Köppen-Geiger climate map of Europe). Mean annual precipitation in all sites is estimated at ~820 mm with mean January and July temperature approximately 3°C and 18°C, respectively. The land use change gradient consists of four study sites and has been selected based on historical and current land cover. Three sites have been under perennial forest (Ronquères, dominated by >80% F. sylvatica and Q. robur sp.), pasture (Blégny) and cropland (Velm) for at least 240 years. One site, i.e. the recently converted cropland (Ganspoel) has only been managed as cropland since 1980 at the earliest and has had a monoculture of maize (Z. mays L.) for the last 14 years; before, the land was mainly used as intensive pasturing. Cropland periods of forest cover. The old cropland (Velm) is dominated by a rotation system with maize, wheat (T. aestivum) and fodder beets (B. vulgaris). Catchment sizes range between 34 and 230 ha (see Supplementary Table S1 for details on the land use change gradient).

Multiple soil parameters were analysed on soil cores of at least one meter (Supplementary Table S2–4; Supplementary Table S6, S9): soil bulk and clay mineralogy, pH (H$_2$O), particle size distribution, cation exchange capacity, biogenic Si in soils, Si adsorbed onto Fe and Al (hydr)oxides and major elemental content in soil (Al, Si, Fe, Ca, K, Na, Mg, Mn, Ti). All analyses were conducted on dried soil samples (at least 3 days at 75°C).

#### Soil water sampling

Soil water was collected using Teflon suction cups (Eijkelkamp) along two topographical transects in the landscape (hollow and ridge concavity), at three locations (valley, slope and plateau) and at three soil depths (30, 60 and 90 cm) (see Supplementary Fig. 1). Sampling occurred on a monthly basis at base flow (see Supplementary Fig. S1). Soil water sampling was placed close to the stream are continuously fed by shallow groundwater from aquifers (seeps). Soil water collected from the riparian zone within the forest was similarly mixed with deep and shallow groundwater, and only suction cups located higher on the slope collect water from the unsaturated zone (Supplementary Fig. S1).

#### Si isotopic analysis

Organic matrices were removed using thermal and aerobic decomposition. The solution was further purified using a cation exchange resin$^{27}$ and Si recovery and cation removal was checked after purification by ICP-MS. Si isotopic compositions were measured with a Nu Plasma Multi-Collector-ICP-MS (Nu Instrument) operating in dry plasma mode. Mass bias was corrected through an external Mg doping$^{28}$. The sample-standard bracketing technique was used to correct for the long-term instrumental drift. All results have been measured as $\delta^{30}\text{Si}$ relative to NBS28 quartz standard (National Institute of Standard and Technology, reference 8546) or an equivalent in-house standard (Pro-Analyse Quartz from Merck) following:

$$\delta^{30}\text{Si} = \left(\frac{^{30}\text{Si}}{^{28}\text{Si}}\right)_{\text{sample}} \times 10^{3} - 1 \times 10^{3}$$

Matrix effects were corrected for by acidoding$^{29}$. The acid doped matrix of NO$_3$-, Cl$^-$, SO$_4^{2-}$ and PO$_4^{3-}$ was adjusted to 500 mg L$^{-1}$, 100 mg L$^{-1}$, 200 mg L$^{-1}$ and 50 mg L$^{-1}$, respectively. All samples were replicated in different analytical sessions distributed over several months and all samples were fully replicated at least once. The accuracy of the DSI $\delta^{30}\text{Si}$ measurements was checked on a daily basis by measuring a secondary reference material of known isotopic composition (diatomite)$^{30}$. Long-term average analytical reproducibility on sample full replicates and accuracy on this reference measurement for $\delta^{30}\text{Si}$ was $\pm 0.14\%$ (1σ). On a $\delta^{30}\text{Si}$–$\delta^{30}\text{Si}$ plot (Supplementary Fig. S3) all samples define (R$^2 = 0.985$) a mass-dependent fractionation line $\delta^{30}\text{Si} = \delta^{30}\text{Si}^0 + 0.5108x$, closer to kinetic fractionation ($\beta = 0.5092$) than to an equilibrium fractionation ($\beta = 0.5178$). On the same samples used for Si isotopic analysis, DSI concentrations (molybdnum-blue colorimetric method) and concentration of major cations (K$^+$, Na$^+$, Mg$^{2+}$, Ca$^{2+}$, Al$^{3+}$; Mn$^{2+}$; ICP-MS) were measured (Supplementary Table S12).

#### Statistics

Statistical tests were performed using IBM SPSS package. One-way ANOVA and Scheffe test for multiple comparisons were conducted to test mean differences in DSo $\delta^{30}\text{Si}$ between sites, depths within sites, seasonal variation within sites and distance to river within sites. If the assumption of normality (Shapiro–Wilk statistic) was not supported, or group variances were not homogenous (Levene test statistic), alternative statistics to test mean differences and multiple comparisons were used (i.e. Welch ANOVA and Games–Howell test). Details on the statistical tests can be found in Supplementary Table S8 and S9.

1. Sommer, M., Kaczorek, D., Kuzyakov, Y. & Breuer, J. Silicon pools and fluxes in soils and landscapes - a review. *J. Plant Nutr. Soil Sci.* 169, 310–329 (2006).
2. Cornelis, J. et al. Tracing the origin of dissolved silicon transferred from various soil-plant systems towards rivers: a review. *Biogeochemistry* 8, 89–112 (2011).
3. Calverton, C., Marschel, C., Harl, T. & Turpault, M. P. Rapid clay weathering in the rhizosphere of Norway Spruce and oak in an acid forest ecosystem. *Soil Sci. Soc. Am. J.* 73, 331–338 (2009).
4. Hinsinger, P., Fernandes Barros, O. N., Benedetti, M. F., Noack, Y. & Callot, G. Plant-induced weathering of a basaltic rock: experimental evidence. *Geochim. Cosmochim. Acta.* 65, 1337–1352 (2001).
5. Epstein, E. Silicon. *Annu. Rev. Plant Physiol. Plant Physiol.* 50, 641–664 (1999).
6. Hodson, M. J., White, P. J., Mead, A. & Broadley, M. R. Phylogenetic variation in the silicon composition of plants. *Ann. Bot.* 96, 1027–1046 (2005).
7. Derry, L. A., Kurtz, A. C., Ziegler, K. & Chadwick, O. A. Biological control of terrestrial silica cycling and export fluxes to watersheds. *Nature* 433, 728–731 (2004).
8. Carey, J. C. & Fulweiler, R. W. The terrestrial silica pump. *Plos One* 7, e52932 (2012).
9. Struyf, E. & Conley, D. Emerging understanding of the ecosystem silica filter. *Biogeochemistry* 107, 9–18 (2012).
10. Treguer, P. J. & De La Rocha, C. L. The world ocean silica cycle. *Ann. Rev. Mar. Sci.* 5, 477–501 (2013).
11. Frings, P. et al. Lack of steady-state in the global biogeochemical Si cycle: emerging evidence from lake Si sequestration. *Biogeochemistry* 117, 255–277 (2014).
12. Conley, D. J. et al. Deforestation causes increased dissolved silicate losses in the Hubbard Brook Experimental Forest. *Global Change Biol.* 14, 2548–2554 (2008).
13. Struyf, E. et al. Historical land use change has lowered terrestrial silica mobilization. *Nature Communications* 1, 129 (2010).
14. Laruelle, G. et al. Anthropogenic perturbations of the silicon cycle at the global scale: Key role of the land-ocean transition. *Global Biogeochem. Cy.* 23, GB4031 (2009).
15. Carey, J. C. & Fulweiler, R. W. Human activities directly alter watershed dissolved silica fluxes. *Biogeochemistry* 111, 125–138 (2012).
16. Clymans, W., Struyf, E., Govers, G., Vandenbeere, F. & Conley, D. J. Anthropogenic impact on amorphous silica pools in temperate soils. *Biogeochemistry* 8, 2281–2293 (2011).
17. Gunzter, F., Keller, C., Poulton, P. R., McGrath, S. P. & Meunier, J.-D. Long-term removal of wheat straw decreases soil amorphous silica at Broadbalk, Rothamsted. *Plant Soil* 352, 173–184 (2012).
18. Vandevenne, F., Struyf, E., Clymans, W. & Meire, P. Agricultural silica harvest: have humans created a new loop in the global silica cycle? Environ. Sci. Technol. 10, 243–248 (2012).

19. Keller, C., Guntzer, F., Barboni, D., Labreuche, J. & Meunier, J. D. Impact of agriculture on the Si biogeochemical cycle: Input from phytolith studies. C. R. Geosci. 344, 739–746 (2012).

20. Collignon, C., Renger, J. & Turpault, M. P. Seasonal dynamics of Al- and Fe-bearing secondary minerals in an acid forest soil: influence of Norway spruce roots (Picea abies (L.) Karst.). Eur. J. Soil Sci. 63, 392–602 (2012).

21. Cornelis, J. T. et al. Silicon isotopes record dissolution and re-precipitation of pedogenic clay minerals in a podzolic chronosequence. Geoderma 235–236, 19–29 (2014).

22. Cornu, S., Montagne, D., Hubert, F., Barre, P. & Caner, L. Evidence of short-term clay evolution in soils under human impact. C. R. Geosci. 344, 747–757 (2012).

23. Cornelis, J. T. et al. Tracing mechanisms controlling the release of dissolved silicon in forest soil solutions using Si isotopes and Ge/Si ratios. Geochim. Cosmochim. Acta. 74, 3913–3924 (2010).

24. White, A. F. et al. Biogenic and pedogenic controls on Si distributions and cycling in grasslands of the Santa Cruz soil chronosequence, California. Geochim. Cosmochim. Acta. 94, 72–94 (2012).

25. Ding, T., Wan, D., Wang, C. & Zhang, F. Silicon isotope compositions of dissolved silicon and suspended matter in the Yangtze River, China. Geochim. Cosmochim. Acta. 68, 205–216 (2004).

26. Ding, T. P. et al. Silicon isotope fractionation between rice plants and nutrient solution and its significance to the study of the silicon cycle. Geochim. Cosmochim. Acta. 72, 5600–5615 (2008).

27. Opfergelt, S. & Démel, P. Silicon isotopes and continental weathering processes: Assessing controls on Si transfer to the ocean. C. R. Geosci. 344, 723–738 (2012).

28. Cockerton, H. E. et al. Stable-isotope (H, O, and Si) evidence for seasonal variations in hydrology and Si cycling from modern waters in the Nile Basin: implications for interpreting the Quaternary record. Quat. Sci. Rev. 66, 4–21 (2013).

29. Ziegler, K., Chadwick, O. A., Brzeziński, M. A. & Kelly, E. F. Natural variations of 63Si/Si ratios during progressive basalt weathering, Hawaiian Islands. Geochim. Cosmochim. Acta. 69, 4597–4610 (2005).

30. Savage, P. S., Georg, R. B., Williams, H. M. & Halliday, A. N. The silicon isotope composition of the upper continental crust. Geochim. Cosmochim. Acta. 109, 384–399 (2013).

31. Ziegler, K., Chadwick, O. A., White, A. F. & Brzeziński, M. A. δ30Si systematics in a granitic saprolite, Puerto Rico. Geology 13, 817–820 (2005).

32. Delstanche, S. et al. Silicon isotopic fractionation during adsorption of aqueous monomeric acid onto iron oxide. Geochim. Cosmochim. Acta. 73, 923–934 (2009).

33. Odze, M., von Blanckenburg, F., Hoedl, D., Dietzel, M. & Bouchet, J. Si stable isotope fractionation during adsorption and the competition between kinetic and equilibrium isotope fractionation: Implications for weathering systems. Chem. Geol. 380, 161–171 (2014).

34. Ding, T. P. et al. Silicon isotope fractionation in bamboo and its significance to the biogeochemical cycle of silicon. Geochim. Cosmochim. Acta. 72, 1381–1395 (2009).

35. Clymans, W. et al. Temporal dynamics of bio-available Si fluxes in a temperate forested catchment (Meerdaal forest, Belgium). Biogeochemistry 116, 275–291 (2013).

36. Blecker, S. W., McCulley, R. L., Chadwick, O. A. & Kelly, E. F. Biologic cycling of silica across a grassland bioclimosequence. Global Biogeochem. Cy. 20, GB5023 (2006).

37. Bartoli, F. & Wilding, L. P. Dissolution of Biogenic Opal as a Function of its Physical and Chemical Properties. Soil Sci. Soc. Am. J. 44, 873–878 (1980).

38. Oltava, P. et al. The effect of organic matter on chemical weathering: Study of a small tropical watershed: Nsimi-Zoetele site, Cameroon. Geochim. Cosmochim. Acta. 63, 4013–4035 (1999).

39. Herbillon, A. I. [Chemical estimation of weatherable minerals present in diagnostic horizons of low activity clay soils] Proceedings of the 8th International Clay Classification Workshop: Classification, Characterization and Utilization of Oxisols (part 1) [Beinroth, F. H., Camargo, M. N. and Eswaran (eds.)] [39–48] (Rio de Janeiro, 1986).

40. Delvaux, C. et al. Controls on riverine δ30Si signatures in a temperate watershed under high anthropogenic pressure (Scheidt - Belgium). J. Marine Syst. 128, 40–51 (2013).

41. Sommer, M. et al. Si cycling in a forest biogeoecosystem - the importance of transient state biogenic Si pools. Biogeosciences 10, 4991–5007 (2013).

42. Matichkenov, V. V. & Bocharnikova, E. A. [The relationship between silica and soil physical and chemical properties] Silica in Agriculture [Datnow, L. E., Snyder, G. & Korndörf, G. (ed.)] (Elsevier, Amsterdam, Netherlands, 2001).

43. Opfergelt, S., Burton, K. W., Koppe von Strandmann, P. A. E., Giselson, S. R. & Halliday, A. N. Riverine silicon isotope variations in glaciated basaltic terrains: Implications for the Si delivery to the ocean over glacial-interglacial intervals. Earth Planet. Sci. Lett. 369–370, 211–219 (2013).

44. Georg, R. B., Reynolds, B. C., Frank, M. & Halliday, A. N. New sample preparation techniques for the determination of Si isotopic compositions using MC-ICPMS. Chem. Geol. 235, 95–104 (2006).

45. Abrahams, K. et al. delta Si-30 and delta Si-29 determinations on USGS BHVO-1 and BHVO-2 reference materials with a new configuration on a nu plasma multi-collector ICP-MS. Geostand. Geoanal. Res. 32, 193–202 (2008).

46. Cardinal, D., Alleman, L. Y., de Jong, J., Ziegler, K. & Andre, L. Isotopic composition of silicon measured by multicollector plasma source mass spectrometry in dry plasma mode. J. Anal. Atom. Spectrom. 18, 213–218 (2003).

47. Huysges, H. et al. Effect of seasonal biogenic silica variations on dissolved silicon fluxes and isotopic signatures in the Congo River. Limnol. Oceanogr. 56, 551–561 (2011).

48. Reynolds, B. C. et al. An inter-laboratory comparison of Si isotope reference materials. J. Anal. Atom. Spectrom. 22, 561–568 (2007).

49. Georg, R. B., Reynolds, B. C., West, A. J., Burton, K. W. & Halliday, A. N. Silicon isotope variations accompanying basalt weathering in Iceland. Earth Planet. Sci. Lett. 261, 476–490 (2007).

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Author contributions
F.I.V. collected the samples and wrote the first drafts. C.D. and H.H. optimised and developed the isotopic analytical method, analysed the samples, made the data processing, and C.D., H.H. and J-T.C. co-developed the discussion. F.I.V., W.C., E.S., G.G. and B.R. were involved in site selection and/or installation of the land use gradient. B.R. and A.L.B. provided background data on clay analysis and Si fractions in the soil. P.M.E., L.A. and G.G. initialised and conceptualised the work on Si biogeochemistry in joint collaborations. All authors contributed to the writing and methodological development of the paper.

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CORRIGENDUM: Landscape cultivation alters δ³⁰Si signature in terrestrial ecosystems

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The original Article contained an error in the calculation of the weathering index Total Reserve in Bases (TRB) in figure 2b. The correct figure 2 appears below as Figure 1.
Figure 1 | (a) Scatterplot of biogenic silica (BSi) in mg g\textsuperscript{-1} dry soil in the soil profile, (b) Total Reserve in Bases (TRB = [Na] + [Mg] + [Ca] + [K]) weathering index calculated on dry soil, in cmol charge kg\textsuperscript{-1}. Sites are represented by symbols: Ronquières (circles), Blégny (stars), Ganspoel (triangle) and Velm (crosses). Multiple symbols within a site in (b) represent different TRB values calculated from positions and depths along the slope in every site for which soil water DSi\textsubscript{d} \textsuperscript{30Si} are available, i.e. 3 in forests, 6 in pasture, 5 in young cropland and 7 in old cropland (See supplementary information for details).