

Below we list the changes in the manuscript that we have done in response to the comments of the three Referees. For a full explanation of our response to the Referees and our decisions we refer to our previous response to the Referees. In some cases their comments were quite general, e.g. the request to be more to the point, and in this case our response is probably best seen in the comparison of the old and the new manuscript below.

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Referee #1:

General comments:

The abstract has been rewritten following the suggestions mainly of Referee #1 (see below). The manuscript has been shortened by removing certain passages and sentences. We have also tried to avoid repeating the impact of riparian soils and the enrichment there too much and made clarifications where Referees have pointed out that it is needed (see details below). In some cases entire passages have been rewritten for improved clarity.

Small overall comments:

Two figures were removed, as suggested by Referee #1.

15 Referee #1 thought that the title was a bit long. We have now proposed a shorter title.

It is not easy to find datasets to compare our data with, but Referee #1 especially pointed out the data published by Lidman et al. (2014). We have made a comparison to that data, which can be seen in Fig. 6. It is not obvious to us how further comparisons between these two datasets could be made.

20 *Specific comments:*

1. The reasons for investigating a large group of element has been stated in the abstract: i) many of the investigated elements have not previously been investigated in riparian soils, ii) inclusion of a wide range of elements with contrasting biogeochemical properties makes it easier to see what processes that are important in the riparian zone.
2. We now tried to emphasize the role of TOC and organic matter in the abstract.
- 25 3. The abstract has been entirely rewritten following the comments of the three Referees. The two final sentences have been removed.
4. Lines 3-5 state that the riparian zone can affect water quality. Lines 11-13 were meant to state that small streams are important of the runoff generation even in large catchments and that they therefore are important to study. This has been clarified. Lines 13-15 have been removed and the reference has been moved to line 3-5.
- 30 5. Lines 23-25 were deleted.
6. We have added examples of why some of the unexplored elements are important, but it would be a very long description if we were to go through each of the 32 elements. Furthermore, the purpose was not to study each of these elements in detail, but to make a broader study of the chemistry of the riparian zone.

7. We have tried to emphasize that the main reason for using a multi-element approach was to obtain a more overarching understanding of the riparian zone and the processes that are happening there. We have added a reference to a previous study, where it was possible to predict the behavior of different elements based on their fundamental chemical properties.
- 5 8. The flow pathways were identified using hydrological tracers. This has been added to the manuscript. An overview of the transect is shown in Fig. 1. A cross section of the transect is shown in Fig. 2, where the flow pathways are illustrated in the bottom subplot.
9. More information on the soils has been added with a more detailed description of where the lysimeters are located. However, because S22 is the only soil profile with distinct soil horizons, S22 is described more thoroughly than S12 and S4.
- 10 10. Information about the depth of the organic layer in S22 has been added. There are soil maps of the area, but since all soils in the catchment are classified as till, they are not very useful. Apparently, the organic riparian soils have not been considered to be important. I have colleagues, who are trying to develop models that can predict the width of the riparian zone, but so far we have no verified map that can be published.
- 15 11. The information about the porosity has been moved to where the differences in hydraulic conductivity are discussed. That should make it clearer why the porosity is discussed. Information about the sampling depth was added the figure caption. It has also been added that the median and quartiles refer to the measurements that were done every 20 m along the stream that drains the investigated transect.
- 20 12. The site description has been changed so that it now starts with more general information and then describes the transect, as suggested by Referee #1.
13. A cross section of the transect is shown in Fig. 2. The bottom subplot illustrates the relationship between discharge and groundwater levels. We have added a reference to Fig. 2 in the second paragraph of 2.2, which Referee #1 was referring to, and stated that it shows the groundwater levels in the transect at different discharge.
- 25 14. Given that one of the major concerns of the Referees was that the manuscript should be shortened we have not proceeded with an ANOVA of the vertical trends. Since we do not know how to generalize those results, we fear that it would result in a lengthy discussion. As illustrated by Fig. 2, the main trend in the dataset is the lateral variation so in order to keep the manuscript more concise we believe that it is best to focus on that trend.
15. Figs. S6 and S7 have been removed, as suggested.
16. Table 1 has been updated with the requested information.
- 30 17. Since one of the major objectives of the revision was to shorten the manuscript and if possible reduce the number of figures, we have left Fig. S4 in the supplementary material. It is an interesting figure, but we feel that in comparison with the other figures in the manuscript it is less important because it only illustrates a single element instead of a more general trend.
- 35 18. The title of section 3.6 has been changed to “the role of riparian soils in the boreal landscape”, since Referee #1 thought that the original title was misleading. In addition, parts of the section has been removed or rewritten. We believe that the text now is more to the point and better justifies the title.
19. “More or less” has been removed. Throughout the manuscript we have also tried to use more precise formulations.

Technical corrections:

- 40 T1: The justification of the names has been removed as requested.
- T2: The error has been corrected.

T3: As far as we can see, Fig. S1 is first introduced on the line before Fig. S2 is introduced so it should be correct (p. 4, line 22).

T4: Loss on ignition (LOI) was added to the caption of Fig. S1.

T5: The sentence has been moved to the beginning of the paragraph and rewritten.

5 T6: The passage about pH was shortened so the mistake in question has been removed.

Referee #2:

The presentation of the data has been revised. Many parts of the manuscript have been removed or rewritten as shown below. In particular we have tried to make the text less repetitive and more to the point, as requested by all Referees. This should be
10 apparent from the comments in this document, but also from the comparison of the old and the new version of the manuscript.

Specific comments:

Page 1, line 9: The reference to lakes has been removed.

15 Page 1, line 10: "More or less" has been removed.

Page 1, line 21: The abstract has been rewritten. We have tried to clearly state problem and briefly describe how the measurements were done. Information about the site has been added to the abstract.

Page 2, line 5: These lines have been rewritten. We have tried now tried to emphasize that the riparian zone is important both for the aquatic systems (water quality) and for the terrestrial systems (fate of nutrients, pollutants etc.).

20 Page 3, line 5: This part of the manuscript has been rewritten. We have now tried to be clearer about the background and the purpose of the study.

Material and methods

25 Site description: The site description has been changed following the suggestion of Referee #2, starting with a general description of the area and then a more detailed description of the transect.

Fig. 1: It is clearly stated in the manuscript that the study was conducted in one of the subcatchments of the Krycklan catchment (as shown in Fig. 1). The nested approach often used in the Krycklan Catchment Study is, however, not relevant for this study, since it was conducted in one single catchment. Since the manuscript was criticized for having too many figures, it seems hard to motivate the inclusion of a map of the entire Krycklan catchment, in which the subcatchments in
30 question hardly would be visible. (It is one of the smallest ones.) Local soil maps classify all soils as till so they can unfortunately not be used to distinguish or illustrate the riparian zone. Therefore, we cannot supply such a map.

Page 3, line 18: We have now written that the direction of the groundwater was determined using hydrological tracers.

Page 3, line 25: A reference to Fig. S2 has been included as suggested. We also added a reference to Grabs et al., who made a broader investigation of organic matter in riparian soils in Krycklan.

Page 3, line 26: As we replied in our previous comments, mor is a type of humus, which is typical for coniferous forests. It now says “so-called mor” to emphasize that it refers to the thin organic layered discussed in the same sentence. We have checked the term, and it can easily be googled by readers who want to know more about it, so we chose to keep it in the revised manuscript.

Page 3, line 32: The sentence has been rephrased.

Page 4, line 2: A reference is given to Fig. S2, in which the LOI is given.

Page 4, line 31: The sampling has been described in more detail in “2.2. Sampling and analyses”. It has also been explicitly stated that water was sampled both from the saturated and from the unsaturated zone.

Page 5 (?), line 13: We have now stated that the loggers, which normally are used to monitor the groundwater levels were out of order during the sampling period. We have also explicitly stated the correlations between discharge and groundwater levels are based on previous research and that the groundwater levels were estimated based on the discharge data.

Page 5, line 23: The relationship was established by one of the co-authors in a previous study, but the results have not been published. Hence, Fig. S3 is the proper reference.

Page 6, line 5: The reference to the definition was already given in the manuscript, but now we have also explained more explicitly what Ω means.

Page 6, line 6: We have added information about the PCA: the parameters were scaled and centered, but no rotation was used. We have also added that all statistical analyses except the regression in Fig. S4 were done using average concentrations.

Page 6, line 10: Following the recommendations of Referee #3 the section about concentrations in biota has been substantially shortened. Nevertheless, we have tried to properly introduce the questions that these measurements were meant to address, namely the concerns that the enrichment of many potentially toxic elements in the riparian zone also might lead to elevated concentrations in riparian biota. Because the strong enrichment of many potentially toxic elements in the riparian zone was not known previously, we are not aware of previous publications that have addressed this question so no such references have been added.

General comment: We have been careful to cite previous publications whenever we refer to previous measurements or previous conclusions concerning the transect. The results of this study are strictly speaking the numbers presented in Tables 1 and S4. However, an important part of the analysis of this data is to put it into the context of previous research and to try to combine all that is known about this system into a coherent picture. Some of the conclusions we present may therefore rely on data both from this study and data from previous studies combined. The manuscript does not have separate sections for results and discussion, as requested by Referee #2. We found that disposition unsuitable for this manuscript because some of the measurements, for instance the effect on biota, rely heavily on the conclusions from other measurements, e.g. the strong

enrichment in the riparian soil water. Therefore, we would prefer to keep the manuscript with combined section for Results and Discussion.

Table 1: We have added the requested information to Table 1. As for the temporal trends, we believe that it goes beyond the scope of this manuscript, where the idea was to give an overview of the data. We cannot see how we possibly could cover that much data in single manuscript because we have so far not found any way to generalize the temporal trends in a similar manner as the spatial trends.

Fig. 2: The bottom subplot shows the approximate groundwater levels at different discharge exactly as stated in the original manuscript – not the hydraulic conductivity. We have added that this is based on Laudon et al. (2004) in the figure caption.

Page 7, line 3: There was an error here, but the entire passage has been rewritten and shortened.

Page 7, line 8: The observed enrichment of Fe in riparian soil water is a result of this study. However, these results are discussed in the light of previous studies on Fe in this transect and in the Krycklan area. We have rewritten much of the passage about Fe so it should be clearer how these previous results relate to our results. One important conclusion is that the riparian soils are responsible for the absence of Fe colloids in the headwater streams.

Page 7, line 19: We have removed the information about the nine principal components and only focused on the two first ones, which later are shown in the biplot. As we make no further analyses using the principle components, we have not used the Kaiser criterion. Since one of the main messages of the Referees was that we should shorten the manuscript, we have not proceeded any further with the PCA.

Page 7, line 25: As we see it, the role of the PCA is to justify the focus on the lateral trends in the transect. One could possibly argue that this is obvious given the results, but since we make a substantial simplification by just looking at the ratio between the average concentrations in S4 and S22, respectively, we believe that it is a good idea to justify this statistically. The biplot illustrates this is a good way. Instead of focusing more on the PCA, we believe that it is better to focus on the more mechanistic explanations that are developed in the following sections of the manuscript.

Page 13, line 1: This chapter has been shortened and partly rewritten, trying to avoid repetitions and being more to-the-point, as requested by all Referees. We bring up the questions that Referee #2 mentions in the discussion, but as we said in our previous comments, we do not think that those questions can be answered based on the data we present in this manuscript. Therefore, we have to leave these questions about weathering and transport unanswered for future projects.

Referee #3:

Uncertainties in pH:

We state in the manuscript that the average prediction error is 0.24 pH units. The relationship between the modelled and the measured pH is illustrated in Fig. S4. pH was not included in any statistical analyses such as the PCA, which now also is

stated in the manuscript. The passage about pH has been shortened given the limitations of modelled values, as suggested by Referee #3.

Biological uptake:

- 5 Referee #3 noted that that it was incorrect to refer to “uptake in biota”. In the revised manuscript this expression has been removed. Instead we refer to “concentration in biota”, which is what we measured. As suggested by Referee #3, the section has been significantly shortened (ca. 40%), and much of the text has been rewritten. We have also tried to explain more clearly in the revised manuscript why concentrations in biota were measured.
- 10 Concerning the organic content of the soils the LOI (loss on ignition) for the three soil profiles is shown in Fig. S1. The variation in organic matter along the stream is further illustrated in Fig. S2.

Acronyms:

- The acronym REE has been explained in the revised in the manuscript. The acronym TOC is explained in both the abstract
15 and the manuscript. The explanations were added at the first mentioning of these acronyms, not necessarily those pointed out by Referee #3.

Organic content:

All mentioning of “organic content” have been replaced by “content of organic matter” or a similar expression.

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From soil water to surface water – how the riparian zone controls ~~the element~~ transport ~~of major and trace elements~~ from a boreal forest to a stream

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10 **Abstract.** ~~The riparian zone is the narrow strip of land, which lines lakes and watercourses. In the boreal region the riparian zone of headwaters often tends to be wetland like with high concentrations of organic matter, low pH and more or less reducing conditions. This means that riparian soils in many respects are different from the podzols and other types of mineral soils that dominate the boreal landscape. In this study a large number of major and trace elements (Al, As, B, Ba, Ca, Cd, Cl, Co, Cr, Cs, Cu, Fe, K, La, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Si, Sr, Th, Ti, U, V, Zn, Zr) and other parameters such as sulphate, total organic carbon (TOC) and pH were analysed in groundwater and soil water in a boreal hillslope. The objective was to investigate how the chemistry changes as the groundwater passes through the riparian zone and enters the stream. Boreal headwaters are often lined by strips of highly organic soils, which are the last terrestrial environment to leave an imprint on discharging groundwater before it enters a stream. Because these riparian soils are so different from the podzol soils that dominate much of the boreal landscape, they are known to have a major impact on the biogeochemistry of important elements such as C, N, P and Fe and the transfer of these elements from terrestrial to aquatic ecosystems. For most elements, however, the role of the riparian zone has remained unclear, although it should be expected that the mobility of many elements are affected by changes in, for example, pH, redox potential and concentration of organic carbon as they are transported through the riparian zone. Therefore, soil water and groundwater was sampled at different depths along a 22 m hillslope transect in the Krycklan catchment in northern Sweden using soil lysimeters and analysed for large number of major and trace elements (Al, As, B, Ba, Ca, Cd, Cl, Co, Cr, Cs, Cu, Fe, K, La, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Si, Sr, Th, Ti, U, V, Zn, Zr) and other parameters such as sulphate and total organic carbon (TOC). The results showed that the concentrations of most investigated elements increased substantially (up to 60 times) as the water flowed from the uphill mineral soils and into the riparian zone, largely as a result of higher TOC concentrations. The stream water concentrations of these elements were typically somewhat lower than in the riparian zone, but still considerably higher than in the uphill mineral soils, which suggests that riparian soils have a decisive impact on the water quality of boreal streams. The degree of enrichment in the riparian zone for different elements could be linked to the affinity for organic matter, indicating that the pattern with strongly elevated concentrations in riparian soils is typical for organophilic substances. One likely explanation is that the solubility of many organophilic elements increases as a result of the higher concentrations of TOC in the riparian~~

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zone. Elements with low or modest affinity for organic matter (e.g. Na, Cl, K, Mg and Ca) occurred in similar or lower concentrations in the riparian zone. Despite the elevated concentrations of many elements in riparian soil water and groundwater no increase in the concentrations in biota could be observed (bilberry leaves and spruce shoots).

Most of the investigated elements displayed substantially higher (up to 60 times) concentrations in the riparian soils than in the uphill mineral soils. There were also examples of nearly uniform concentrations throughout the transect (e.g. Na and Si), but in only a few cases were lower concentrations observed in the riparian zone (e.g. K, Mg and Ca). The degree of enrichment in the riparian soils could be linked to the affinity for organic matter, indicating that the pattern with strongly elevated concentrations in riparian soils is typical for organophilic elements. However, the elevated concentrations of many elements in the riparian zone could not be linked to increased uptake in biota (bilberry leaves and spruce shoots). In summary, the results confirmed that the riparian zone plays a central role for regulating the stream water quality and the transfer of a wide range of elements from terrestrial to aquatic ecosystems. Hence, riparian soils are essential for understanding the fate of nutrients, pollutants and other substances in the boreal landscape.

1 Introduction

The riparian zone is the interface between the terrestrial landscape and the streams and rivers draining it. Hence, the riparian soils are often the last material that the groundwater is in contact with before it becomes surface water. Although it normally occupies only a minor fraction of the total catchment area, it can therefore have a disproportionately high impact on the water quality of streams, rivers and lakes over wide spatial scales (1-1,000 km²) (Billett and Cresser, 1992). ~~Similarly, it may also exert the ultimate control over the fluxes of many nutrients, pollutants and other substances from the terrestrial to the aquatic ecosystems due to its strategic location in the landscape;~~ Smart et al., 2001; Seibert et al., 2009). ~~Likewise, because of its strategic location in the landscape, the riparian soils may also exert the ultimate control over the fate and transit times of nutrients, pollutants and other substances in the terrestrial ecosystems.~~ The importance of the concept of the riparian zone hinges on the fact that riparian soils can be profoundly different from the uphill soils that dominate the landscape (Sauer et al., 2007). In the boreal region shallower groundwater levels and generally wetter conditions tend to prevail in the vicinity of stream channels (Grabs et al., 2012). As a result, there is often an accumulation of organic matter, ~~especially along small streams,~~ which creates more wetland-like conditions in the riparian zone. ~~Because of the importance of small streams for~~ This is particularly common along smaller streams, which despite their size contribute significantly to the runoff generation ~~the presence of organic-rich riparian soils has far-reaching consequences for the water quality of boreal lakes and water courses even in large rivers in force of their number~~ (Bishop et al., 2008; Lassaletta et al., 2010). ~~The geochemistry of the riparian zone has been shown to be an important predictor for the stream water quality over wide spatial scales (1-1,000 km²)~~ (Smart et al., 2001). In the case of carbon the significance of the riparian zone is well-established both when it

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comes to dissolved organic carbon (DOC) and CO₂ (e.g. Fiebig et al., 1990; Hinton et al., 1998; Oquist et al., 2009; Lyon et al., 2011; Winterdahl et al., 2011; Grabs et al., 2012; Knorr, 2013; Fraser Leith, 2014; ~~Ledesma et al., 2015~~Ledesma et al., 2015). However, the special biogeochemical conditions of the riparian zone also have consequences for the transport of widely different substances such as nitrogen (Hill, 1996; Cirimo and McDonnell, 1997; Sabater, 2003), phosphorus (Mulholland, 1992), base cations (Ledesma et al., 2013), aluminium (Cory et al., 2007), mercury (Bishop et al., 2009), persistent organic pollutants (Bergknut et al., 2011) and pesticides (Vidon et al., 2010). Furthermore, the riparian zone is gaining increasing recognition as an ecological hotspot (Jansson et al., 2007; Kuglerová et al., 2013; Nilsson et al., 2013). As a consequence, precautions are often taken in modern forestry in order to reduce the deleterious impact of logging on riparian soils (Moore and Richardson, 2012; Kuglerová et al., 2014; Tiwari et al., 2016). ~~Good arguments have also been put forward that the riparian zone is a key to understanding the temporal variability of stream water chemistry (Seibert et al., 2009).~~

~~However, for~~For the vast majority of elements, ~~however~~, the role of the riparian zone remains unexplored. Yet, there are good reasons to hypothesise that the riparian soils influence the transport of many more substances than the above given examples. In the boreal region the mobility of many ~~elements~~metals and miscellaneous hydrophobic substances is strongly connected to the presence of organic matter, both by accumulation in peat and other forms of solid organic matter (e.g. González et al., 2006; Cloy et al., 2009; Lidman et al., 2013) as well as by transport by organic colloids and particles (e.g. Gustafsson et al., 2000; Dahlgvist et al., 2007; Pokrovsky et al., 2010). The ~~often elevated accumulation of~~ organic ~~content of matter in the riparian soils in comparison to normal forest soils~~zone is also associated to fundamental chemical parameters such as pH and redox potential, which are well-known to influence the speciation and mobility of many elements. The purpose of this study was therefore to broaden the perspective on riparian soils by investigating the behaviour of a wider range of elements as they are transported across the chemical gradients of the riparian zone in a boreal hillslope transect, starting in an uphill podzol profile and following the chemical evolution of the groundwater all the way to the stream. ~~By using a multi-element approach, comprising 32 different elements plus TOC, sulphate and pH, we hypothesised that it might be possible to identify some of the key processes that govern the behaviour of various substances in the riparian zone. In order to also capture the temporal variability in~~One reason is that each of the 32 elements (plus TOC and sulphate) included in this study are important *per se*, for instance as micronutrients (e.g. Se, Ni, Cu, Zn, Mn), as pollutants (e.g. Cd, V, Cs, U, As), as tracers for important processes (e.g. Cl, Zr) etc. More importantly, however, a multi-element approach to the riparian chemistry, which allows a comparison of different elements with contrasting or corresponding biogeochemical properties, can first and foremost help identify the most important processes taking place in the riparian soils and contribute to a more over-arching understanding of the functioning of riparian soils. In the best case, it can also help us predict how various substances will be affected based on their biogeochemical properties (Lidman et al., 2014). In order to capture the temporal variability in the soil water and groundwater chemistry along the transect samples were collected at ten sampling occasions between January and October, covering the hydrologically most active period at the studied site. This approach resulted in a

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large amount of data so the intention here is not to discuss any of the investigated elements in particular detail, but rather to provide a general description of how the water chemistry changes with respect to various types of elements as the water passes through the riparian zone. We believe that a better appreciation of the riparian zone is important for assessing both the water quality and the long-term mass balance of the boreal landscape with respect to weathering products, pollutants, nutrients and other substances.

2 Material and methods

2.1 Site description

The ~~investigated hillslope is located~~ study was conducted in the Krycklan catchment in northern Sweden (Laudon et al., 2013). ~~It drains to~~ The investigated transect is located by a small first order stream (0.12 km² km⁻²), referred to as Västrabäcken or C2 in previous publications. ~~The stream water sampling site is located ca. 300 m downstream of the investigated transect and is, which is one~~ of the main sites included in the Krycklan Catchment Study (Figure 1). The local climate is cold temperate with an mean annual temperature of 1.8°C (1981-2010), ranging from -9.5°C in January to 14.7°C in July (Laudon et al., 2013). The mean annual precipitation is 614 mm, of which roughly half is lost by evapotranspiration and half by runoff. The snow cover remains for 168 days per year on average (1980-2007), varying in maximum depth between 43 cm and 113 cm. The maximum soil frost depth varies between 2.5 cm and 79 cm (1993-2007) depending on factors such as temperature and the timing and depth of the snow (Haei et al., 2010). The entire catchment is covered by century-old coniferous forest, mainly Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*), with elements of deciduous trees and shrubs.

The soils in the Västrabäcken catchment are made up by locally derived till, mostly several meters deep (such as by the investigated transect). The mineralogy is dominated by quartz (40%), K-feldspar (25%), plagioclase (23%), amphibolites (7%), muscovite (4%) and chlorite (1%) (Ledesma et al., 2013). The transect consists of three sampling sites located 4 m, 12 m and 22 m, respectively, from the stream as measured along the flow pathway of the groundwater. The perpendicular distance to the stream is considerably shorter than this, less than 2 m for the closest site. The transect is sometimes referred to as the S transect in previous publications so the three sites are therefore called S4, S12 and S22, respectively. At each site suction lysimeters were installed in 1995, allowing regular sampling of soil water and groundwater from different depths in the three soil horizons. In this study four depths in S4 and five depths in S12 and S22, respectively, were sampled. The different lysimeters are referred to as S4, S12 and S22 followed by the depth in centimetres. For example, S22-90 means that the water was sampled 22 m from the stream at a depth of 90 cm. S22 is an iron podzol with clearly developed soil horizons. As such it is probably typical for most of the investigated catchment and in a broader sense also for boreal forests in general. At the surface there is a thin organic layer (mor), but apart from that the organic content is low (<0.8% below 10 cm) (Table S1). As the groundwater approaches the stream the podzols gradually give way for more organic histosols as a result of the

increasingly wet conditions closer to the stream channel. S4 and S12 can both be considered to represent the riparian zone, while S22 in contrast represents a more ordinary forest soil. The thickness of the organic layer increases from 20–30 cm in S12 to ca. 80 cm in S4. At ca. 1 m, however, there is a compact layer of basal till with substantially lower hydraulic conductivity than shallower soil horizons (Fig. S1). The porosity of the soils also varies (36–83%) with higher values in more organic layers and, consequently, a decline with depth in all profiles (Table 2). The continuation of the transect further upstream from S22 varies somewhat depending on the hydrological conditions, but the distance to the water divide is ca. 100–120 m (Fig. 1). The transect has low relief with an inclination of ca. 3%, as compared to the average slope of the entire catchment (C2), which is 8.7%. The accumulation of organic matter is typical for the riparian zone of this catchment (Fig. S2).

The soils in the transect are made up by several meters of glacial till, but at a depth of ca. 1 m there is a compact layer of basal till with low hydraulic conductivity (Fe! Hittar inte referenskälla.S2; Bishop, 1991; Bishop, 1991). Previous investigations of the hydrology in the transect have indicated that most of the water transport takes place in above this compact till layer (Rodhe, 1989; Laudon et al., 2004; Peralta-Tapia et al., 2014). At all three sampling sites along the transect (S4, S12 and S22) there is clear relationship between the groundwater levels and the discharge in the stream (Seibert et al., 2009). The discharge increases exponentially with rising groundwater levels following the so-called transmissivity feedback mechanism, suggesting that much of the water transport takes place the uppermost saturated soil layers (Bishop et al., 2011).

The mineralogy is dominated by quartz (40%), K-feldspar (25%), plagioclase (23%), amphibolites (7%), muscovite (4%) and chlorite (1%) (Ledesma et al., 2013). The transect as well as the catchment as a whole is covered by century-old coniferous forest, mainly Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*), with elements of deciduous trees and shrubs. The climate is cold temperate with an mean annual temperature of 1.8°C (1981–2010), ranging from –9.5°C in January to 14.7°C in July (Laudon et al., 2013). The mean annual precipitation is 614 mm, of which roughly half is lost by evapotranspiration and half by runoff. The snow cover remains for 168 days per year on average (1980–2007), varying in maximum depth between 43 cm and 113 cm. The maximum soil frost depth varies between 2.5 cm and 79 cm (1993–2007) depending on factors such as temperature and the timing and depth of the snow (Haei et al., 2010).

The stream channel was deepened, partially straightened and probably also extended further up in the catchment by manual ditching in the 1920s. Ditching of forests was a common practise in Fennoscandia at this time, and a large portion of the Swedish headwaters have therefore been affected in a similar way (Dahlstrom et al., 2005). The purpose was to improve the drainage, thereby counteracting the paludification and increasing the forest productivity. Exposed roots of some older trees in the riparian zone testify that there may have been a lowering of the ground level as a result of the ditching. Presumably peat, which had been building up under the previously wetter conditions, has begun to decay, causing the ground surface to sink by ca. 2–3 dm/20–30 cm in some places.

5 The investigated transect is located ca. 300 m upstream of the catchment outlet and consists of three sampling sites (S4, S12 and S22) located 4 m, 12 m and 22 m, respectively, from the stream as measured along the flow pathway of the groundwater, which was identified using hydrological tracers (Fig. 1). At each sampling site ceramic suction lysimeters were installed in 1995, allowing regular sampling of soil water and groundwater at different depths in the three soil horizons. In this study 10 four depths at S4 and five depths each at S12 and S22 were sampled. Each lysimeter is referred to by the name of sampling site followed by the depth in cm, e.g. S4-45. S22 represents an iron podzol with clearly developed soil horizons. As such it is typical for most of the investigated catchment and in a broader sense also for boreal forests in general. At the surface there is a ca. 8 cm thick organic layer (so-called mor), but apart from that the content of organic matter is low (<0.8% below 10 cm) (Fel! Hittar inte referenskölla.S1). The uppermost lysimeter (S22-20) is located at the lower end of the E horizon, which reaches from 8-20 cm. Then there are three lysimeters (S22-35, S22-50 and S22-75) in the B horizon, which has a hardpan around 75 cm. Finally, there is one lysimeter in the C horizon (S22-90), which starts at ca. 80 cm. This lysimeter is also located in the compact basal till with notably lower conductivity (Table S2). As the groundwater approaches the stream the podzol gradually gives way for more organic histosols as a result of the increasingly wet conditions closer to the stream. S4 and S12 can both be considered to represent the riparian zone and lack any distinct soil horizons. The thickness of the organic layer increases from 20-30 cm at S12 to ca. 80 cm at S4 (Fel! Hittar inte referenskölla.S1). This accumulation of organic matter in the riparian zone is typical for this and other headwaters in the Krycklan catchment (Fig. S2; Grabs et al., 2012). The slope is not particularly steep with an inclination of ca. 3%, which can be compared to the average inclination of the Västrabäcken catchment, 8.7%. Uphill from S22 the slope continues ca. 100-120 m to the water divide (Figure 1). Previous research has demonstrated that in all three soil profiles (S4, S12 and S22) there is a clear relationship between the groundwater level and stream discharge (Laudon et al., 2004; Seibert et al., 2009). The discharge increases exponentially with rising groundwater levels following the so-called transmissivity feedback mechanism, which suggests that much of the water transport takes place the uppermost saturated soil layers (Fig. 2; Bishop et al., 2011). This is also related to the porosity of the soils, which varies from 36-83% with higher values in more organic soils and, consequently, a decline with depth in all profiles (Fel! Hittar inte referenskölla.). Further details on the transect can be found elsewhere in previous 25 publications (Nyberg et al., 2001; Stähli et al., 2001).

2.2 Sampling and analyses

Soil water and groundwater (i.e. both from the saturated and the unsaturated zone) was collected from the lysimeters at ten occasions during 2008 by attaching vacuum bottles to the tubes that are connected to each of the ceramic cups in the soils. The investigation period started during winter baseflow conditions in January and ended in October, when the system again had returned to winter baseflow conditions. Samples were collected every month with the exception of June, when two samples were collected, and September, which was omitted. This sampling strategy was assumed to capture the most active period both in hydrological and biogeochemical terms. This means that there are in most cases ten observations from each depth in each profile, but in certain cases there are values missing either because sufficient amounts of water could not be

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collected due to soil frost or ~~draught~~drought or because the concentrations of some elements in some cases were below detection limit.

In S4 four lysimeters were sampled, reaching from 35-65 cm in depth. This ~~cover~~covers the most hydrologically dynamic part of the profile, since S4-35 never was saturated, except possibly briefly in connection with the peak flow of the spring flood, and S4-65 was constantly saturated, except for a few weeks in the middle of the summer. In S12 five lysimeters covering a depth from 20-70 cm were sampled. S12-20 is believed never to have been saturated, while the groundwater level occasionally may have fallen below S12-70 during the driest parts of the summer. In S22 five lysimeters reaching from 20-90 cm were sampled. Except in connection with the peak flow of the spring flood S22-20 is expected to have been above the groundwater table, whereas S22-75 and S22-90 are expected to have been in the saturated zone throughout the entire sampling period. ~~The~~Approximate groundwater ~~tables~~levels at ~~different discharge are shown in the three-bottom subplot of Fig. 2. As the groundwater loggers were out of order during the sampling sites S4, S12 and S22 period, the groundwater levels~~ were reconstructed using continuous discharge measurements ~~from the form a nearby downstream stream location station, where a pressure transducer continuously measures the water height at a V-notch weir (Fig. 1; Seibert et al., 2009). Previous research has shown that the groundwater levels in all three soil profiles are correlated to the discharge (Laudon et al., 2004)~~Laudon et al., 2004). ~~With~~Hence, the discharge data was used to estimate the groundwater levels using slightly revised ~~regressions the~~regression from Laudon et al. (2004) with R^2 values ~~were of~~ 0.96 (S4), 0.94 (S12) and 0.87 (S22), respectively ($p < 0.001$). ~~Discharge was measured ca. 300 m downstream from the transect at V notch weir using a pressure transducer connected to a data logger (Fig. 1; Seibert et al., 2009).~~

The chemical analyses included Cl, sulphate, ~~POC~~total organic carbon (TOC), Al, As, B, Ba, Be, Ca, Cd, ~~rare earth elements (REEs,)~~ Co, Cr, Cs, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Si, Sr, Th, Ti, Tl, U, V, Zn and Zr. Because of the large similarities between the REEs only La is presented in this study in order to save space and make graphs and tables clearer and more manageable. The fractionation within the lanthanide series will for this reason have to be addressed elsewhere. pH was not directly measured in the water samples from 2008, but ~~older~~based on previous measurements ~~in this transect (1996-1998) have established~~there is a strong relationship between pH on one hand and TOC and Ca on the other (Fe! Hittar inte referenskälla.S3), which was used to estimate the pH of the analysed water samples in this study. The average prediction error was 0.24 pH units. Additional analyses of water from the adjacent stream (referred to as C2 or Västrabäcken in previous studies) were taken from the material presented by Lidman et al. (2014).

The soil water and groundwater was sampled by attaching vacuum bottles to the lysimeters for 2-3 days. The lysimeters were carefully installed in 1995 so any effects of disturbance on the soils were expected to have evanesced. The samples were filtered (0.45 μm) and acidified to $\text{pH} < 2$ with ultrapure double-distilled HNO_3 . TOC was then analysed by a Shimadzu TOC-VCPH instrument. Previous research in Krycklan has demonstrated that the amount of particulate organic carbon rarely

exceeds a few percent in these systems so ~~the total organic carbon (TOC)~~ is essentially equal to the dissolved organic carbon (DOC) (Laudon et al., 2011). Anions were measured by ion chromatography (Dionex ICS-90, Sunnyvale, Ca, USA; 4 mm i.d. AG14 and AS14 columns) using a suppressor and conductivity detector. All other elements were analysed by ICP-MS (Perkin-Elmer ELAN 6000).

The speciation of elements in the riparian soil water was calculated using thermodynamic modelling in Visual MINTEQ 3.1 (Gustafsson, 2012). The binding to DOC was modelled using the Stockholm Humic Model as described by Sjostedt et al. (2010). ~~Following~~The modelled association to DOC (in %) was then used as an index for the affinity for organic matter (Ω) based on the definition suggested by Lidman et al. (2014) ~~the modelled association. An element with Ω close to DOC was used as an index for the~~100% is considered to have strong affinity for organic matter (Ω), ~~whereas an element with Ω close to 0% is considered to have low affinity for organic matter.~~ In ~~one~~ regression analysis Ω was transformed using the logit function:

$$\text{logit}(\Omega) = \log\left(\frac{\Omega}{1-\Omega}\right) \quad (1)$$

All statistical analyses, including the principal component analysis (PCA), were made in R (R Core Team, 2014). In order to remove all missing values Cr and Th were excluded from the PCA of the soil water and groundwater and one value each for U and Zr were interpolated from the two surrounding lysimeters (Table 1). ~~Because pH was modelled it was not included in the PCA. The variables were scaled and centred, but no rotation was used. All statistical analyses were done using average concentrations except in Fig. S4.~~

The biological uptake in the riparian zone and in the upslope soil, respectively, was tested by collecting fresh bilberry leaves (*Vaccinium myrtillus*) and spruce shoots (*Picea abies*) early in the growing season (11 June 2013). Two grouped samples of each species were collected in the vicinity of the lysimeters at S4 and S22, respectively. A screening of the element concentrations were made using ICP-MS at a commercial laboratory (ALS Global, Luleå, Sweden) following certified standard procedures. We report the results for the 19 elements, which were measured with an accuracy of two of more significant digits.

3 Results and discussion

3.1 Soil water and groundwater chemistry

For most elements there was a substantial increase in the concentrations along the transect, from the upslope profile (S22) to the riparian profile (S4) (Table 1, ~~Fel! Hittar inte referenskölla.~~). These patterns, which were persistent throughout the

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year, are exemplified by TOC and V in Figure 2. In the case of TOC the increase in riparian soil water and groundwater (up to 33 mg L⁻¹ on average) was not surprising given that the organic content of organic matter in the riparian soils are is substantially higher (up to 33 mg L⁻¹ on average) than the in upslope soils, which typically contained only a few mg L⁻¹ (Fell Hittar inte referenskälla.S1). This is a trend, which appears to be is typical for the riparian soils of many small boreal streams (Grabs et al., 2012). V followed that same trend as TOC with substantially higher (nearly two orders of magnitude) concentrations in the riparian zone. However, there were also elements, whose concentrations did not increase markedly in the riparian zone. One such example is Na, which occurred in relatively stable concentrations around 2 mg L⁻¹ throughout the entire transect. Further examples (Ca, Al, La, K, Fe and Mn) can be found in Figs. S6 and S7, where Al, La, Fe and Mn all exhibit similar patterns as TOC and V. In the case of Al, this confirmed previous studies in this transect (Fig. 2). (Cory et al., 2007).

pH was estimated to be on average 4.5 in S4, ranging from 4.2-4.7 with slightly higher values in deeper horizons: on average 4.3 in S4-35 as compared to 4.6 in S4-64. In S12 the pH was on average 5.0, covering an interval from 4.4 to 5.2. Again there was a tendency of higher pH in deeper horizons. The average pH in S22 was only slightly higher than in S12, 5.1, but there was a notable difference of more than one pH unit between S22-90, which had an average pH of 5.9, and the upper horizons, which had an average of 4.8. Due to the stable pH in all profiles of S22 this also coincides with the observed range in pH, 4.8-5.9. Hence, the pH gradient experienced by pH was estimated to decrease from S22 (on average 5.1) to S4 (on average 4.5) with generally increasing pH with depth in all profile and a maximum of 5.9 in S22-90. Hence, the pH gradient experienced by the substances transported from the uphill podzol to the riparian zone is approximately in the order of 0.5-1 pH units unit. This shift in pH alone may, however, have palpable consequences for the speciation of many metals and the solubility of solid phases such as Al(OH)₃ and various Fe precipitates (Gustafsson, 2001; Sauer et al., 2007; Sjostedt et al., 2010), and even more so especially when combined with the increase in TOC concentration (Figure 2). In the case of Al, the average concentrations in the investigated lysimeters ranged from 1.6 µg L⁻¹ in S22-35 to 1700 µg L⁻¹ in S4-35 – a difference of more than three orders of magnitude. Similar trends for Al have previously been observed in this transect (Cory et al., 2007). Detailed studies of the Fe speciation using X-ray absorption spectroscopy (XAS) have revealed considerable complexity with simultaneous presence of both Fe²⁺ and Fe³⁺ throughout the transect Fe was also strongly enriched in riparian soil water with average concentrations ranging from 5.3 µg L⁻¹ at the bottom of the E horizon (S22-20) to 1500 µg L⁻¹ in S4-45. Previous studies using X-ray absorption spectroscopy (XAS) have demonstrated that both Fe²⁺ and Fe³⁺ are present throughout the transect, but in the riparian zone the Fe speciation was completely dominated by organic Fe complexes (Sundman et al., 2014). In S4 the aqueous The dominance of organically bound Fe speciation was completely dominated by organic Fe complexes, which suggests that that in the riparian zone is responsible for consistent with the absence of the Fe colloids in the adjacent stream (Neubauer et al., 2013). Normally This observation is important because Fe colloids are an important vector for many major and trace elements in boreal rivers (Gustafsson et al., 2000; Dahlgvist et al., 2007), but while such Fe precipitates should be present in the upslope podzols the lower pH and higher TOC concentration

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of the riparian zone apparently destabilised or blocked these precipitates from reaching the stream water. Only as the significance of the riparian zone decreased with increasing catchment area, e.g. due to less organic riparian zones and a larger influence of deep groundwater. If no Fe colloids are present, however, organic colloids are likely to play the lead role in transporting more insoluble elements through the riparian zone. Only as the streams become larger, Fe colloids will gradually appear in the stream water (Neubauer et al., 2013). A prerequisite for this is that pH increases with increasing catchment area, while the TOC concentration decreases, which causes both Fe and Al to precipitate (Kohler et al., 2014; Lidman et al., 2014). This is in turn related to less organic matter in the riparian soils of larger streams and an increasing influence from deeper groundwater, which entirely may bypass the riparian soils (Peralta-Tapia et al., 2015; Lidman et al., 2016). ~~will these Fe colloids start to appear in the stream water (Neubauer et al., 2013).~~

3.2 Principal component analysis

In order to further explore the trends in the soil water and groundwater chemistry a principal component analysis (PCA) was conducted (Figure 3). There was a considerable variance in the dataset, and ~~as much as nine principal components were needed to explain more than 95% of it. The~~ the first two principal components could only explain in total 57% of the variance with PC1 contributing with 33% and PC2 with 24%. A noteworthy pattern in Figure 3 is that most lysimeters from the same profile fall close to one another. This suggests that the variance in the transect mainly is horizontal rather than vertical. This underlines the relevance of the concept of the riparian zone, since it demonstrates that the riparian profile (S4) is decisively different from the upslope mineral soil (S22). The only deviations from the division into S4, S12 and S22, respectively, were the deepest lysimeter in S22 (S22-90) and the shallowest lysimeter in S12 (S12-20). In the case of the former, there was a notable decrease in the hydraulic conductivity below ca. 80 cm in S22 (**Fel! Hittar inte referensskälla.**), suggesting that the exchange between S22-90 and shallower soil layers is limited. This lysimeter was for instance characterized by high concentrations of base cations, particularly K, Ca and Mg, and higher pH (Figs. S6 and S7; Table 1). It has been demonstrated that the concentration of base cations in the area tends to increase with the age of the groundwater (Klaminder et al., 2011), which supports the idea that S22-90 represents a less hydrologically active layer. As concerns S12-20, it represents a more organic soil with higher TOC concentrations than the deeper horizons of S12 (Fig. S1; ~~which for instance causes it to have a higher TOC concentration (S1; Figure 2; Table 1).~~).

Most of the elements are found on the same side of the biplot as the S4 lysimeters (e.g. Ba, Cd, Al, Zr and Ni), indicating that they occurred in higher concentrations in the riparian zone. However, some of them (e.g. Li, Co, Si, Cu and Tl) are shifted towards the S12 lysimeters, while others (e.g. Pb, Fe, As, Zn, TOC, Ti and V) are shifted slightly towards the S22 lysimeters. A strong association to the S12 lysimeters is mainly displayed by Mn and Sr, signifying that they occurred in higher concentrations in S12. The S22 lysimeters are surrounded by the alkali metals K, Rb and Cs, but also B and Se. In the case of Se the higher concentrations in S22 may be related to the more oxidising conditions, since the solubility of Se easily

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decreases in more reducing environments (Gustafsson and Johnsson, 1992). The special patterns of Se in the soil water and groundwater are also consistent with the dynamic behaviour of Se concentrations in the adjacent stream (Lidman et al., 2011). Finally, some major ions like Ca, Mg, Na and sulphate are found in between the S12 and the S22 lysimeters in the biplot.

5 3.3 Enrichment in the riparian zone

The grouping of the lysimeters at the same distance from the stream suggests that it is possible to reduce some of the complexity of the dataset by investigating the average concentrations at each of the sites. Since the principal change in the soil water and groundwater chemistry occurred longitudinally along the transect, a comparison of the average concentrations in the riparian zone (S4) to the average concentrations in the upslope mineral soil (S22) can give a fair overview of the major trend in the transect. ~~It has already been observed that many elements occurred in substantially higher concentrations in the riparian zone (Table 1, Fig. 2), but when plotting the ratio of the average concentration in S4 and the average concentration in S22 it becomes evident just how different the riparian zone is from the uphill mineral soil (Fig. 4). For the vast majority of elements the concentrations were considerably higher in the riparian zone. A (Table 1). Figure 4 shows the ratio between the average concentrations in S4 the average concentrations in S22 for all investigated elements. It is clear that for the vast majority higher concentrations were observed in the riparian zone. Only a few elements – most notably K, but also Ca, Mg and Se – showed a contrasting pattern with higher concentrations in the uphill soils, while yet a few others, e.g. Rb, Na and sulphate, occurred in similar concentrations throughout the transect. However, a closer look at the observations (Table 1) shows that the higher average concentrations of K, Ca and Mg in the mineral soil (S22) can be attributed to the deepest lysimeter in S22, which also stood out in the PCA (Figure 3). Thus, excluding this sample from the averages will remove most of the differences between S4 and S22 for K, Ca and Mg.~~

~~Most elements, however, displayed considerably higher concentrations in the riparian zone than in the uphill mineral soil.~~ The far right side of Figure 4, i.e. the elements which are most strongly enriched in the riparian zone, is occupied by metals, which are well-known for their low solubility, e.g. Zr, Th and Al. The most extreme example is V with more than 60 times higher concentrations in the riparian zone than in the mineral soils further up in the transect. Unlike Zr, Th and Al the speciation of V is directly affected by the redox conditions, which may contribute to the differences in its concentrations (Agnieszka and Barbara, 2012). However, it should be noted that the Th concentrations in S22 fell below the detection limit in all but one of the lysimeters: (Table 1). This was the shallowest lysimeter (at 20 cm) with the highest TOC concentration. Therefore, there are good reasons to believe that the enrichment factor (S4/S22) for Th and also Cr were underestimated. -If it is assumed that the Th concentration in S22 is correlated to the TOC concentration or that it follows the same pattern as Zr and V, this would be enough to push the S4/S22 ratio well above 100. ~~However, which element is most enriched and to what degree is perhaps not a crucial issue. More important is to identify what chemical properties cause some elements to occur in elevated concentrations in the riparian soil water and groundwater and others not to.~~

The general impression from both the PCA (Figure 3) and, more specifically, the S4/S22 ratio (Figure 4) is that more insoluble or immobile elements tend to occur in higher relative concentrations in the riparian zone, while generally more mobile elements such as the base cations and anions like Cl and sulphate occur in more uniform concentrations throughout the transect. In boreal waters more immobile elements are often to a large extent transported by colloids, typically Fe colloids or organic colloids, which tend to represent two different colloidal populations (Lyven et al., 2003). As discussed above, the Fe colloids appear to be missing in the riparian zone, leaving only the organic colloids as possible carriers (Neubauer et al., 2013). There is also strong evidence that organic matter is responsible for carrying a wide range of elements in boreal waters (e.g Gustafsson et al., 2000; Pokrovsky et al., 2005; Andersson et al., 2006; Dahlqvist et al., 2007; Pokrovsky et al., 2010; Vasyukova et al., 2010; Aiken et al., 2011). Furthermore, it has been demonstrated that the affinity for organic matter of various metals is essential for understanding their transport and spatial variability in the boreal landscape (Lidman et al., 2014). Using the same definition of the affinity for organic matter as was proposed by Lidman et al. (2014), makes it possible to quantitatively test the hypothesis that the enrichment in the riparian soil water and groundwater was related to the affinity for organic matter. Figure 5 shows the S4/S22 ratio, i.e. the enrichment in the riparian zone (S4) as compared to the upslope mineral soil (S22), as function of the affinity for organic matter. The affinity for organic matter is expressed in percent and represents the proportion of each element that is expected to be bound to DOC in the soil water and groundwater of S4, but in this application it was used mainly as an index for the strength of the affinity for organic matter.

The selection of elements in Figure 5 was based on the analysed elements and the available thermodynamic constants in Visual MINTEQ 3.1 (Gustafsson, 2012). Some elements like Fe and Mn were excluded because uncertainties regarding their oxidation state make the affinity for organic matter ill-defined. U was, however, included as U^{6+} despite its redox chemistry, since any presence of U^{4+} just would increase the already high affinity for organic matter of U^{6+} (>96 %) slightly. As can be seen in Figure 5, where the affinity for organic matter has been transformed using the logit function (**Fe! Hittar inte referensskälla.**), there was a strong positive correlation between the affinity for organic matter and the enrichment in the riparian soil water and groundwater ($r=0.88$, $p<0.01$). The modelling also indicated that many of the elements, which are enriched in the riparian zone, would not be soluble in such high concentrations had it not been for the high TOC concentrations. Yet, Figure 5 cannot be taken as direct evidence that each of the enriched elements in the riparian zone is governed primarily by TOC as there also may be other controlling factors, especially in the uphill podzol profile (S22), where the TOC concentration was low. ~~Yet, our data, but it~~ strongly ~~suggests~~ suggests that TOC is a crucial parameter for understanding the role of the riparian soils.

Although it is beyond the scope of this work to analyse the time series for all the investigated elements in the lysimeters, it is illustrative to look at a few examples that can shed further light on the role of organic matter in riparian soils. Ti is one

example of a relatively insoluble metal, which should have a low mobility unless there is some carrier phase such as TOC present. **Fel! Hittar inte referenskölla.** shows all of the observations of Ti plotted against TOC, revealing a strong positive correlation ($r=0.97$, $p<0.001$) between Ti and TOC for all soil water samples. Clearly, high Ti concentrations were encountered solely in samples with high TOC concentrations.

The significance of TOC was also supported by the temporal variability of organophilic elements in the soil water and groundwater, at least in the more organic soils. One example is Al, which in each of the lysimeters in S4 had a significant ($p>0.05$) positive correlation ($r>0.84$) to TOC when looking throughout the entire sampling period (see details in **Fel! Hittar inte referenskölla.**). At times when TOC increased so did Al, supporting the hypothesis that the mobilisation and transport of organophilic elements in the riparian zone largely could be controlled by TOC. Similar patterns were, however, absent in S22 so the mobility of Al in these inorganic soils was evidently controlled by other processes. For instance, it has been shown that the mobility of Al in the Bs horizon of podzol soils can be limited by the precipitation of $Al(OH)_3$ and in some cases imogolite (Gustafsson, 2001). Hence, while the large differences in TOC concentrations between the uphill mineral soils and the riparian zone were responsible for the elevated levels of many elements in the riparian soil water, this does not necessarily imply that it also controls their mobility in each of the investigated soil layers.

3.4 Influence on the stream water chemistry

The analyses of the soil water and groundwater along the investigated transect demonstrated that the riparian zone can induce considerable changes in the water chemistry. It is therefore pertinent to ask what influence the riparian zone has on the stream water quality. Had there been no differences between the riparian zone and the uphill mineral soils one should expect ~~that~~ the stream water ~~would~~ resemble the groundwater in S22. However, since the groundwater changes character as it ~~approaches the stream and passes through~~ enters the organic riparian soil, one might expect that stream water chemistry instead would resemble the riparian groundwater. ~~As discussed above, the riparian zone is that last terrestrial environment that the groundwater is in contact with before it enters the stream so it could potentially have a disproportionately strong impact on the stream water composition.~~

When comparing the uphill mineral soil (S22) to the stream (C2), many elements (e.g. Th, Al, U, Fe and La) occurred in considerably higher concentrations (up to 60 times) in the stream water than in the soil water (**Fel! Hittar inte referenskölla.6**). Yet, stream water concentrations were missing for some of the metals, e.g. V and Zr, which showed the largest enrichment in the riparian soil water. The difference between the stream water and the uphill soil water is remarkable given that this podzol profile ~~is likely to~~ should be reasonably representative for the vast majority of soils throughout the catchment. For example, rapid degradation of TOC and subsequent precipitation of Fe, Al and associated elements are typical processes in the development of podzols (Gustafsson, 2001; Sauer et al., 2007; Sundman et al., 2014). This illustrates that the riparian zone has a profound impact also on the stream water chemistry for a wide range of elements. ~~Based on Fig.~~

~~5 the effects on the stream water chemistry seem to mainly concern elements, particularly those with a highstrong~~ affinity for organic matter- (Fig. 5).

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5 When comparing the riparian soil water (S4) to the steam water (C2), the concentrations were in many cases ~~even~~ higher in the riparian soil than in the stream (up to 4-5 times). In other words there was no perfect match between the riparian soil water and the stream water (**Fel! Hittar inte referensälla.**). However, the riparian soil water in this study represents only a single transect, whereas the ~~streamsstream~~ water displays an integrated signal for the entire catchment. Although the overall appearance and functioning of the investigated transect should be representative for the catchment at large, there is also a longitudinal variation in the composition of the riparian zone along the stream. For example, the riparian zone of the
10 investigated transect represented an area with higher ~~content of~~ organic ~~eontent~~carbon (around the 3rd quartile) than most reaches of the stream (**Fel! Hittar inte referensälla.** and S2). If the interpretation that the organic matter is controlling the transport of these elements is correct, that could explain why the studied riparian zone exhibited higher concentrations than the stream. Differences in the ~~organic~~ content of organic matter in the riparian zone along the stream is known to derive from variations in the topography and the groundwater flow pathways (Tiwari et al., 2016). This hypothesis is also supported by
15 the fact that the TOC concentrations in the riparian zone ~~also~~ were higher than in the stream (**Fel! Hittar inte referensälla.**).

20 There were only three elements, Ca, Mg and K, which displayed the opposite pattern: higher concentrations in the stream water (C2) than in the riparian soil water (S4) (**Fel! Hittar inte referensälla.**). These three elements also stood out in the measurements in the transect because they occurred in higher concentrations in the mineral soil (S22) than in the riparian soil (S4), mainly due to the high concentrations in the deepest lysimeter in S22 (Figure 4). In the case of Ca and Mg, the agreement between the mineral soil water (S22) and the stream water (C2) was good, whereas the K concentration in the stream water was more than twice as high as in the mineral soil water. K and ~~possibly, to some extent~~ Rb were the only examples of elements with notably higher concentrations in the stream water than in the three soil profiles. The higher
25 concentrations of base cations like K, Ca and Mg in the stream water could indicate a contribution of deeper groundwater to the stream, but at the same time related weathering-products such as Sr, Na, Rb, Cs and Si all showed relatively uniform concentrations throughout the transect and the stream. It is possible that the differences again are ~~eause~~caused by longitudinal heterogeneities along the stream.

3.5 Biological uptake

It has been shown that the 3.5 A hotspot for transfer of pollutants to biota?

Higher species richness ~~of~~ in the riparian zone ~~is higher along~~ of stream reaches with high groundwater discharge. ~~Hence, is a clear sign that the ecological community can benefit from the transport~~flow of nutrients ~~to and through~~ into the riparian zone ~~evidently has ecological consequences~~ (Kuglerová et al., 2013). ~~The results~~ However, not only nutrients, but also a large ~~range of this study have demonstrated that organic soils~~potentially toxic substances, ~~tend to accumulate~~ in the riparian zone also can have nearly two orders of magnitude higher concentrations of certain elements than normal forest soils. It is therefore pertinent to ask whether ~~there also is an elevated accumulation in~~ riparian zone ~~also is a hotspot~~biota, which ~~could constitute an important exposure pathway~~ for biological uptake of natural, but undesirable, elements or anthropogenic pollutants.

~~hazardous substances.~~ The screening of bilberry leaves ~~and spruce shoots~~ from the riparian forest (near S4) and the uphill forest (near S22), respectively, showed no clear relationship between the concentrations in soil water and the concentrations in biota (~~Fe! Hittar inte referenskälla.~~S4; Figure 77). ~~In other words, the elevated concentrations of many elements in the riparian zone did no lead to higher concentration in bilberry leaves. The results were similar for spruce shoots~~ (~~Fe! Hittar inte referenskälla.~~). Also when considering the more unreliable results for elements, which were only reported with one significant digit (e.g. Sb, Pb, Cr, La, Ti, V and Zr), there were no clear signs of elevated concentrations in riparian biota. (Possible exceptions were, however, As, Co and Mo.) ~~Combined these results suggest that the biological uptake either in general is actively regulated by the plants or that the elements are present as species with low bioavailability. The two possibilities do not exclude each other and may vary from element to element, but according to the discussion above and the modelling of the chemical speciation one should expect a large portion of the elements with elevated concentrations in the riparian soil water to be associated with TOC (Fig. 5). For a wide range of metals it has been shown that their~~One important ~~explanation is probably that elements with high riparian concentrations largely are bound to TOC (Fig. 5). For a wide range of elements it has been shown that the~~ bioavailability tends to decrease when they are bound to organic matter, e.g. Pb (~~Van Sprang et al., 2015~~)(~~Van Sprang et al., 2015~~), U (Trenfield et al., 2011a; Trenfield et al., 2011b), Ni (Weng et al., 2004; Deleebeek et al., 2009), Cu (Deruyter et al., 2014) and Zn (De Schamphelaere et al., 2005). ~~Although there may be differences between species, the general effects on the bioavailability are likely to be similar also for spruce, bilberry and many other plants. Hence, the fairly constant concentrations in biota could be explained by the fact that the concentrations of the most bioavailable chemical species do not differ much between the inorganic uphill soils and the riparian zone. Instead, the enrichment occurs mainly by increasing the amount of the organically bound fractions, which have low bioavailability. In addition, it is possible that the plants are able to regulate the uptake and/or disposal of certain elements.~~

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Considering all ~~While plants growing in the riparian zone generally did not have higher concentrations of elements in both bilberry leaves and spruce shoots that accumulate in riparian soil water, there was, however, one~~ notable exception, displaying a clear enrichment in riparian biota, namely Cs. The soil water concentration exceptions: Cs and Mn. In the case of Cs in the riparian zone was 2-3 times higher than concentrations in the uphill soil, and the concentrations in biota were soil water led to 4-5 times higher. Thus, Cs was the only element, which exhibited more than twice as high concentrations in riparian bilberry leaves (and spruce shoots) as in the uphill ditto. concentrations in biota. Since Cs is considered to have low affinity for organic matter, the ~~general explanation that the elevated element concentrations in the riparian soil water are caused by higher TOC concentrations is unsatisfactory for Cs are probably not directly linked to TOC (Fan et al., 2014). It seems more likely that~~ Instead, factors such as lower amount of mineral surfaces and lower pH might be the reason behind the could allow higher Cs concentration in the riparian zone. In any case, the additional Cs found in the riparian soil water is unlikely to be associated to TOC. Instead, Cs is likely to largely be present as free concentrations of more bioavailable Cs ions in the riparian zone so no effects on the bioavailability from TOC can be expected in this case. There was also one notable example of the opposite, namely lower concentrations in riparian soil water, leading to elevated concentrations in biota. This exception was Mn In the case of Mn the concentrations in riparian biota were lower, which possibly could be related to its redox behaviour, causing Mn to be more present as Mn^{2+} in the riparian zone (Fig. 7) ~~chemistry (Fig. 7).~~

3.6 The ~~importance~~ role of the riparian zone soils in the boreal landscape

The perhaps most important observation in this study was the large differences between the riparian soils and the uphill forest soils ~~for many elements.~~ As discussed above, these differences have previously been known for a ~~few number of~~ elements, but judging from this study the enrichment in riparian soil water is more the water of the riparian zone appears to be a rule more than an ~~the~~ exception (Figure 4). The degree of ~~Since the~~ enrichment in the riparian soil water and groundwater could be linked to the affinity for organic matter (Figure 5), which suggest that), similar enrichment should be expected for many other metals and organophilic substances in general, e.g. organic pollutants (Bergknut et al., 2011). A crucial question then is unavoidably how representative the investigated transect would be over at larger spatial scales. Even in a small catchment like this one (0.12 km²) the chemistry of the draining stream not agree completely with either the water of the riparian zone or that of the uphill mineral soil (Fel! Hittar inte referenskölla.). Given the heterogeneity and complexity of the natural landscape it is doubtful whether it at all would be possible to find something like a representative transect. In all catchments there is likely to be substantial longitudinal and transverse variation in state factors such as topography, grain size distribution and mineralogy, which in turn gives rise to a heterogeneity in hydrology and biogeochemistry (Ledesma et al., 2015). These differences are likely to only increase when trying to compare different catchments to one another. Nevertheless, it was clear that the composition of the stream water had been significantly influenced by the riparian zone, e.g. by gaining substantially higher concentrations of TOC and organophilic elements

Since this study focused on a single hillslope transect, a key question is unavoidably how representative the results are. Needless to say, factors such as topography, hydrology, soil composition etc. will vary from catchment to catchment so there is little reason to expect the exact numbers, e.g. the degree of enrichment of organophilic elements in riparian soils, to repeat themselves. On a more conceptual level, however, (Figure 4). As concerns the stream, in turn, it is known from previous research that it in many respects is typical for forested catchments in the area ~~the gradient represented by this transect from relatively dry organic-poor mineral soils in uphill locations to wetter organic soils near the streams is surely not untypical for the boreal landscape (Sauer et al., 2007; Grabs et al., 2012).~~ Despite their size, small streams and headwaters are fundamental for generating runoff in the boreal landscape (Bishop et al., 2008). If the water quality of these streams and the transfer of TOC and associated elements are controlled by riparian soils, as supported by this study, there are also good reasons to believe that the effects of the riparian soils have implications at much larger scales than the investigated transect (Laudon et al., 2011; Ledesma et al., 2015). The results clearly demonstrated that the riparian zone had a profound impact on the stream draining the transect (Fig. 6), and previous research in the Kryeklan catchment has shown that the water chemistry of this stream (C2) in many respects is typical for forested catchments in the area despite its small size (Cory et al., 2006; Björkvald et al., 2008; Lidman et al., 2012; Köhler et al., 2014; Lidman et al., 2014). Despite their size, small streams and headwaters are important for generating runoff in the boreal landscape, even in large rivers (Bishop et al., 2008). Therefore, on a more conceptual the gradient represented by this transect from relatively dry organic-poor mineral soils in uphill locations to wetter organic soils near the streams is surely not untypical for the boreal landscape (Sauer et al., 2007; Grabs et al., 2012). If the water quality of these streams and the transfer of TOC and associated elements largely are controlled by riparian soils, as suggested by this study, there are also good reasons to believe that the effects of the riparian soils have implications at much larger scales than the investigated transect (Laudon et al., 2011. While riparian soils like the one in S4 are responsible for the high TOC concentrations and the low pH in small streams, they also destabilise many Fe compounds, thereby affecting the balance between organic colloids and Fe colloids, which are the two main carriers in boreal waters (Ledesma et al., 2015). These effects include affecting the balance between organic colloids and Fe colloids, lowering pH and elevating the concentration of TOC and many organophilic elements (Lyven et al., 2003; Neubauer et al., 2013; Köhler et al., 2014; Ledesma et al., 2015). Ledesma et al., 2015).

Arguably, the chemistry of the stream draining the investigated transect did not agree completely with either the water of the riparian zone or that of the uphill mineral soil (Fig. 6). However, given the heterogeneity and complexity of the natural landscape it is doubtful whether it at all would be possible to find something like a representative transect, even in a relatively small catchment like this one (0.12 km²). In all catchments there is likely to be substantial longitudinal and transverse variation in state factors such as topography, grain size distribution and mineralogy, which in turn gives rise to a heterogeneity in hydrology and biogeochemistry (Ledesma et al., 2015). What, then, does the long-term mass-balance for the riparian zone look like? Nevertheless, it was clear that the composition of the stream water had been significantly influenced by the riparian zone, e.g. by gaining substantially higher concentrations of TOC and organophilic elements in general (Fig.

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4). For an element like C, which ultimately is derived from the atmosphere, it is not hard to see how riparian soils can become a major source of TOC to the streams (Fiebig et al., 1990; Agren et al., 2008; Lyon et al., 2011). More intriguing are the associated elements, which in a similar manner as TOC have a major source in the riparian zone. -These elements, however, are largely derived from weathering of local soils, but it is unclear where in the catchment this weathering ~~took~~takes place and what the long-term ~~element budget for the role~~ riparian zone looks like ~~soils play in the boreal landscape~~. One ~~possible explanation would be~~ hypothesis is that there is a preferential net weathering in the riparian zone. This could for instance be related to the higher TOC concentrations and the lower pH as compared to the uphill soils (Erlandsson et al., 2016). This would imply that much of the weathering of organophilic metals is limited to a small fraction of the landscape. Another ~~possibility~~ hypothesis is that these elements initially were released mainly in the upslope mineral soils, which cover much larger areas than the riparian soils, and then have been transported to the riparian zone. Discussing the sources of Al in this transect, Cory et al. (2007) hypothesised that there could be a flushing from uphill mineral soils to the riparian zone in connection with hydrological episodes such as the spring flood. -The results of this study do, however, not support that hypothesis. The Al concentrations in the riparian zone (S4 and S12) were at all sampling occasions throughout the year substantially higher than in the uphill mineral soil (S22) so it seems unavoidable to draw the conclusion that the riparian zone currently is a net source for Al (and other organophilic elements) during all parts of the year. Hence, if one wishes to stick with the hypothesis that the vast part of the weathering of these elements has occurred throughout the catchment, rather than specifically in the riparian zone, one has to assume that most of the organophilic metals, which now are being released from the riparian zone, were brought there and somehow accumulated during some earlier stage, when the riparian zone acted as a sink. For instance, it is possible that organophilic metals historically accumulated in the organic matter of the riparian zone in the same way as they still do in boreal mires (Lidman et al., 2013; Lidman et al., 2014). However, as a result of some change in the system, e.g. the ditching of the stream in the early 20th century, these metals are now being released from the solid organic matter as it decomposes. Under this scenario the current stream chemistry of this and presumably many of all the other ditched streams would represent a historical anomaly. Which ~~explanation~~ hypothesis is true – preferential weathering in the riparian zone or historical accumulation in combination with present mobilisation – seems precarious to answer based on only on the water chemistry throughout the transect. Instead this will require a more detailed investigation of the solid phase as well. A better understanding of the mass-balance of the riparian zone would further elucidate how various substances – nutrients as well as pollutants – are transported from boreal forests to surface waters and help assess the effects of human perturbations such as logging, ditching and climate change on the quality of boreal waters.

4 Conclusions

30 The results of this study demonstrated that riparian soils have a profound effect on the element transport from a boreal forest hillslope to the draining stream, particularly when it comes to elements with a high affinity for organic matter. For some elements the concentrations in the riparian zone were nearly 100 times higher than in the mineral soils less than 20 m

upslope. It could be demonstrated that the degree of enrichment was related to the affinity for organic matter. Whereas elements with low affinity for organic matter occurred in fairly uniform concentrations throughout the transect, elements with a high affinity for organic matter were strongly enriched. This enrichment also had implications for the stream water, which tended to have higher concentrations of ~~DOC~~DOC and organophilic elements than the soil water and groundwater of uphill soils. As a consequence, it can be expected that the water quality of boreal surface waters, especially in smaller catchments and with respect to TOC and organophilic elements, can be quite different from that of the groundwater and soil water throughout most the ~~catchments~~catchment. This emphasises the importance of the riparian zone for understanding the water quality of the boreal landscape and the long-term transfer of solutes from terrestrial to aquatic ecosystems. Despite the strong enrichment of organophilic elements in the riparian soil water no signs of elevated biological-uptakeconcentrations in the riparian zonebiota were observed. At present the riparian zone constitutes a source for a wide range of elements, but further studies are needed to determine the long-term mass-balance of the riparian zone and the underlying causes of the enrichment. The results of this study emphasise that riparian zone is crucial for understanding the long-term fluxes of nutrients and pollutants in the boreal landscape as well as the historical and future water quality of boreal surface waters in the wake of a changing climate and modern forestry.

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15 Data availability

The data will be made available through the homepage of the Krycklan Catchment Study (www.slu.se/Krycklan).

Competing interests

FL and ÅB were funded by the Swedish Nuclear Fuel and Waste Management Company (SKB).

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Table 1. Average element concentrations at different depths in the three investigated soil profiles. All concentrations are given in $\mu\text{g L}^{-1}$ except for TOC, which is given in mg L^{-1} . The number of samples included in the averages varies from 1-10, depending on availability of soil water, detection limits etc. See Fel! Hittar inte referensskälla. for corresponding relative standard deviations. The last column illustrates the enrichment in the riparian zone (the ratio between the average concentration in S4 and S22, respectively).

depth (cm)	S4				S12					S22					Enrichment
	35	45	55	65	20	30	40	60	70	20	35	50	75	90	S4/S22
Al	1700	1400	1200	1400	1200	640	520	410	330	68	1.6	13	8.4	50	81
As	0.95	0.99	0.83	0.60	0.88	0.37	0.22	0.22	0.37	0.057	0.0026	0.19	0.17	0.027	9.4
B	6.3	5.2	4.5	5.1	8.6	5.0	4.3	4.9	4.5	4.2	3.9	3.9	4.4	3.6	1.3
Ba	35	25	25	26	16	16	15	11	10	13	6.0	5.9	6.5	7.8	3.5
Be	0.20	0.16	0.15	0.21	0.17	0.11	0.091	0.099	0.11	0.0098	0.0047	0.0087	0.0080	0.0078	23
Ca	900	1100	1300	1100	810	1600	1800	2000	2100	1100	920	1000	1000	3500	0.73
Cd	0.12	0.16	0.12	0.13	0.061	0.044	0.046	0.070	0.096	0.016	0.012	0.010	0.017	0.0092	10
Cl	1.0	1.1	1.0	1.1	0.99	0.97	0.96	0.97	0.96	0.51	0.72	0.94	0.87	0.79	1.4
Co	1.4	1.5	1.3	1.5	0.70	0.94	1.1	1.1	1.4	0.23	0.11	0.17	0.14	0.027	11
Cr	2.2	1.7	1.4	1.6	1.7	0.75	0.54	0.44	0.40	0.25	n/a	0.15	n/a	n/a	8.6
Cs	0.017	0.022	0.039	0.015	0.075	0.019	0.013	0.011	0.013	0.012	0.0054	0.0074	0.0078	0.010	2.7
Cu	2.3	4.0	2.6	4.5	2.6	2.7	1.8	3.9	3.1	0.84	0.77	0.65	0.51	0.82	4.7
Fe	1400	1500	1300	740	370	110	57	55	160	5.3	74	24	42	43	33
K	110	120	170	100	480	190	150	250	370	360	120	210	210	1000	0.33
Li	3.6	3.2	3.2	3.5	2.6	2.5	2.7	2.7	2.6	0.52	0.48	0.58	1.4	0.67	4.6
La	2.2	1.7	1.6	1.5	1.3	0.87	0.73	1.4	1.6	0.24	0.013	0.088	0.043	0.17	16
Mg	300	380	500	350	420	500	500	590	590	320	310	360	340	1100	0.79
Mn	6.4	9.5	13	8.7	7.4	8.0	7.9	15	21	0.38	0.39	0.22	0.25	3.9	9.1
Na	2200	2000	2100	2000	1900	2000	1900	2100	2200	1500	1700	1900	1900	2400	1.1
Ni	3.0	3.9	3.5	3.7	1.2	1.5	1.7	1.9	2.5	0.83	0.23	0.29	0.30	0.80	7.2
Pb	0.67	0.28	0.29	1.0	0.48	0.18	0.19	0.15	0.11	0.055	0.0018	0.10	0.087	0.15	7.1
pH	4.3	4.5	4.7	4.6	4.4	4.9	4.9	5.1	5.2	4.8	4.8	4.8	4.8	5.9	0.90
Rb	0.79	1.3	1.9	0.71	2.8	1.2	1.0	1.7	2.5	1.9	0.68	0.83	0.82	1.8	0.97
Se	0.15	0.16	0.13	0.15	0.10	0.17	0.19	0.14	0.23	0.032	0.070	0.15	0.86	0.085	0.62
Si	8400	7900	8100	8000	6300	6800	6300	7400	7900	5100	4500	4400	4200	7900	1.6
SO4	4900	5200	5200	5400	4400	4800	5200	5400	5700	3700	3700	4500	4200	8300	1.1
Sr	14	14	14	15	10	17	20	20	20	12	12	9.8	9.7	17	1.2
Th	0.27	0.20	0.18	0.17	0.13	0.067	0.055	0.068	0.084	0.0046	n/a	n/a	n/a	n/a	45
Ti	1.4	1.1	0.83	0.96	0.87	0.38	0.25	0.18	0.20	0.065	0.045	0.076	0.060	0.083	16
Tl	0.028	0.030	0.032	0.021	0.028	0.026	0.017	0.017	0.041	0.0091	0.0038	0.0091	0.0070	0.00094	4.6
TOC	33	24	19	21	26	11	8.5	6.6	5.4	5.2	2.8	1.7	2.0	1.6	9.1
U	0.13	0.093	0.11	0.079	0.084	0.062	0.043	0.092	0.19	0.014	n/a	0.00081	0.00050	0.0095	17
V	2.5	2.7	2.7	2.1	0.97	0.86	0.62	0.28	0.49	0.070	0.036	0.030	0.035	0.032	62
Zn	9.2	12	16	13	15	6.6	6.8	5.6	7.4	6.3	3.1	3.5	4.3	3.4	3.1
Zr	450	300	300	280	220	120	92	120	140	11	0.69	1.8	n/a	16	45

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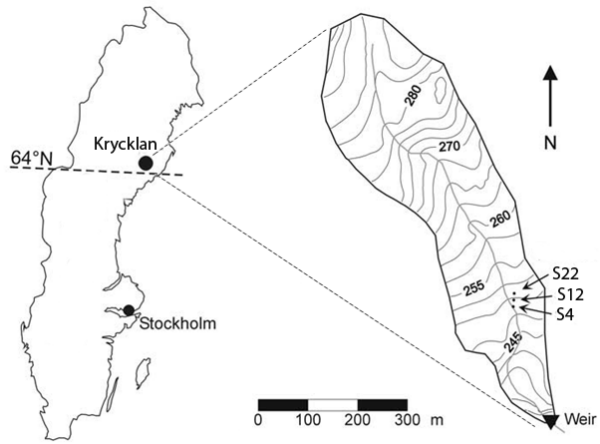
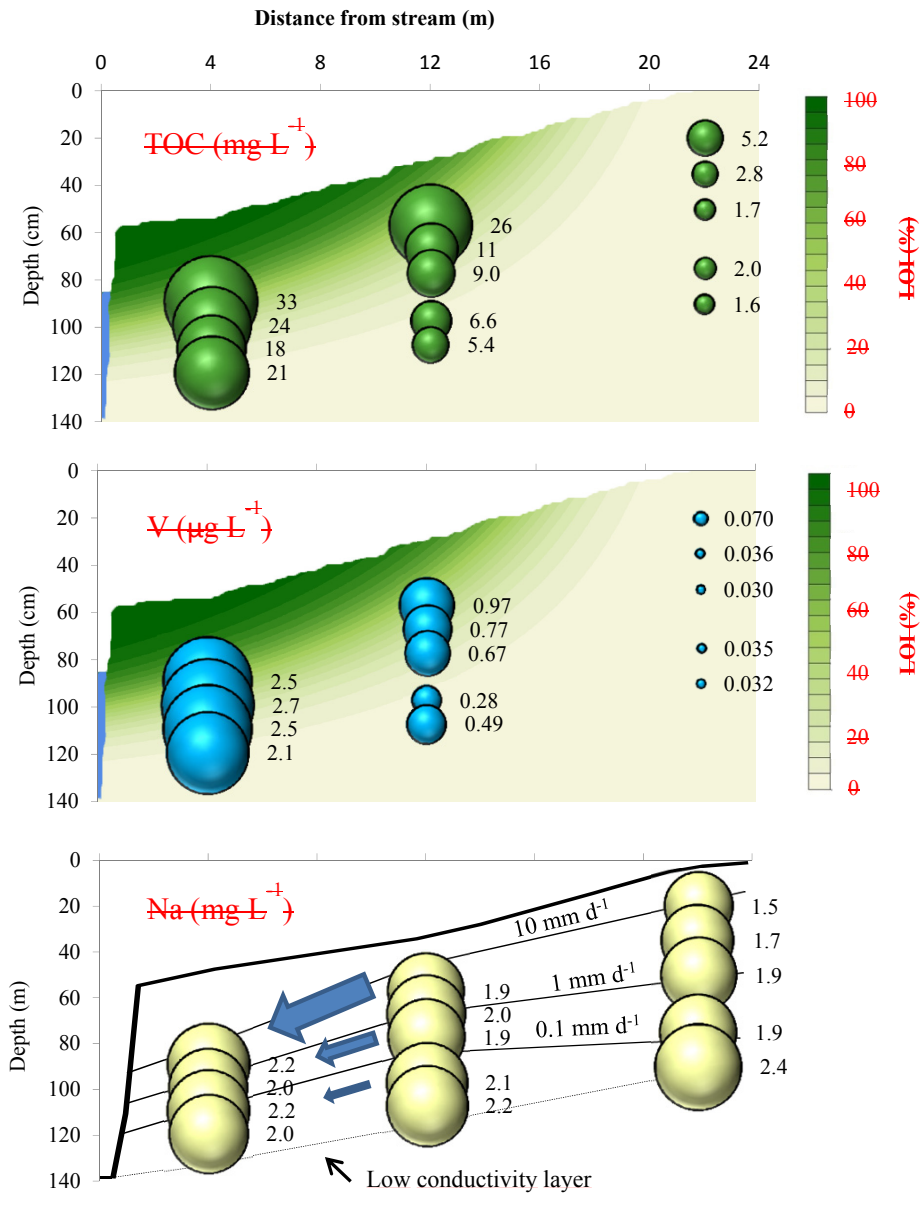


Figure 1. Map of Sweden showing the location of the Krycklan catchment (left) and the Västrabäcken (C2) catchment (right). The location of the sampling sites (S4, S12 and S22) in the investigated transect are shown along with the elevation above sea level (m). Note that the lysimeters are located along the flow direction of the groundwater and not perpendicularly to the stream.



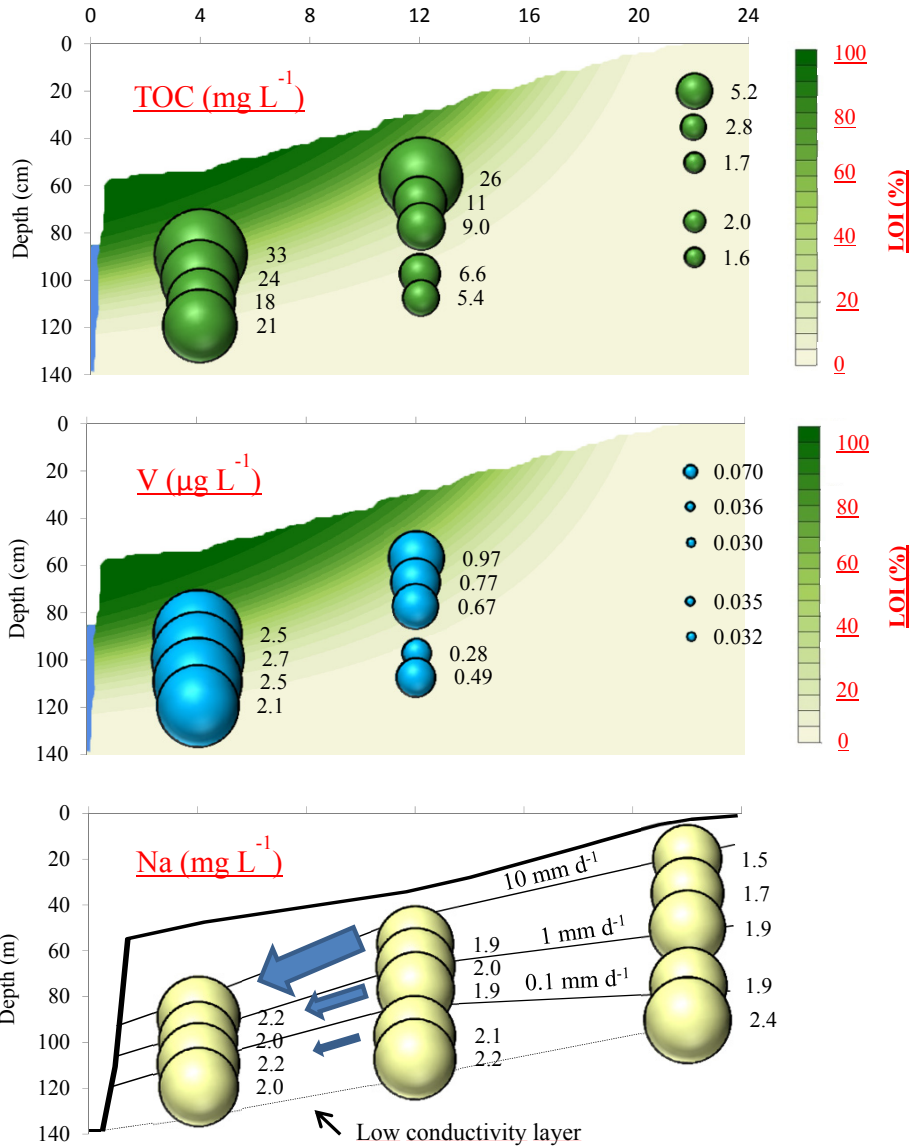
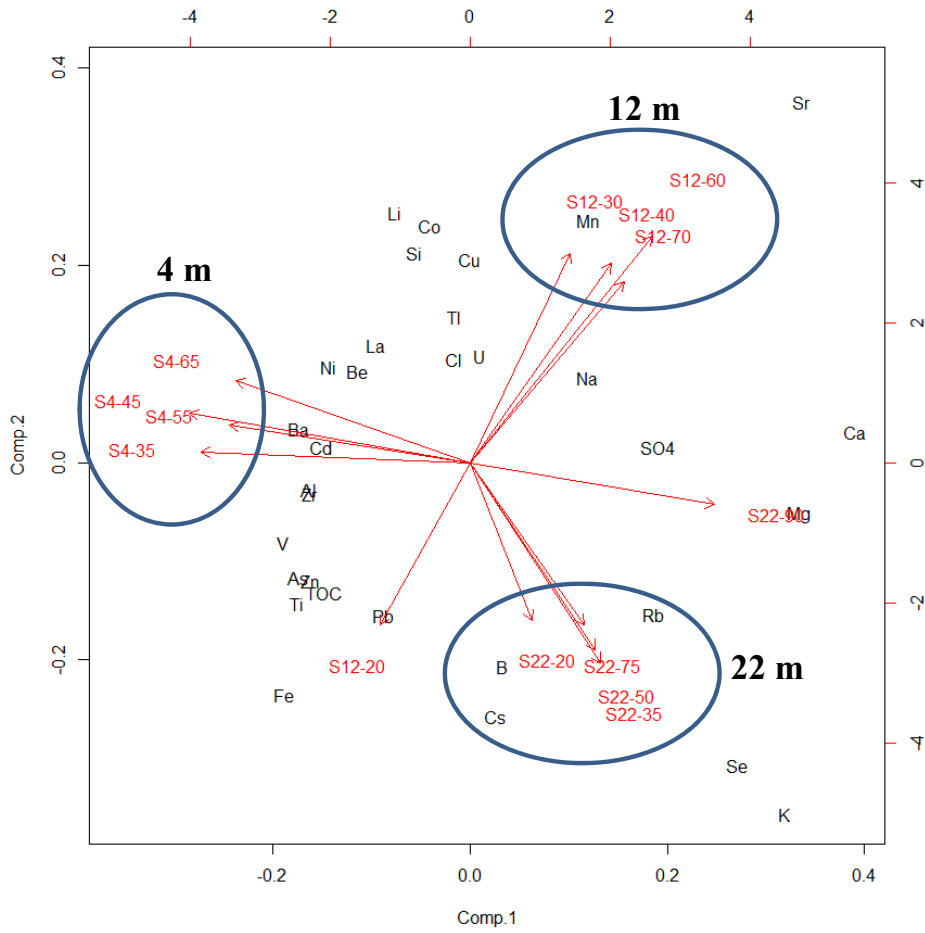


Figure 2. Average soil water and groundwater concentrations of TOC (top), vanadium (middle) and sodium (bottom) in the investigated transect. The area of the bubbles is proportional to the concentration, which in turn is given next to each bubble. The

background illustrates the LOI (%) in the two upper examples. –The bottom subplot illustrates the approximate groundwater levels at different stream discharge: [based on Laudon et al. \(2004\)](#). The distance from the stream is measured along the flow pathway of the groundwater.



5 Figure 3. PCA biplot for the average concentrations in each of the lysimeters. Most lysimeters located at the same distance from the stream ended up close to one another.

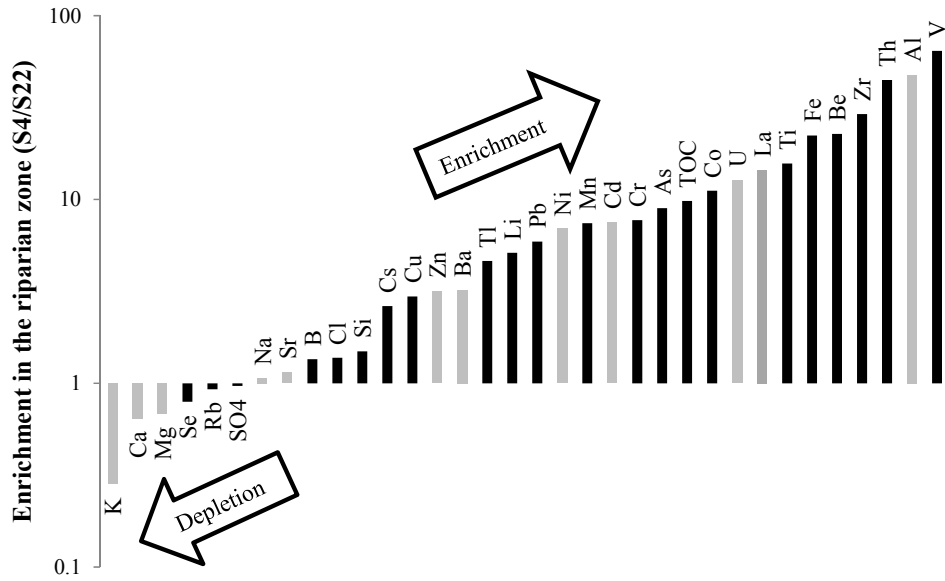
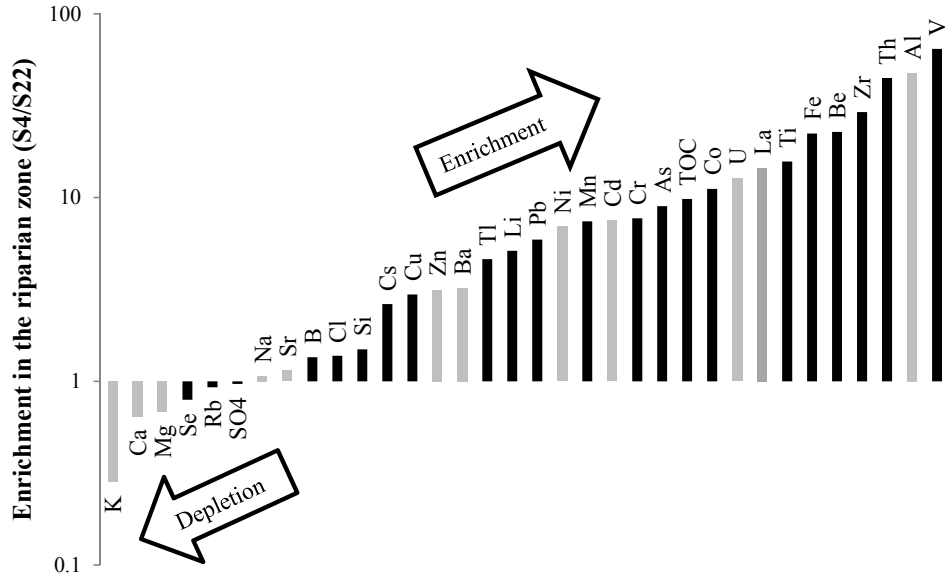
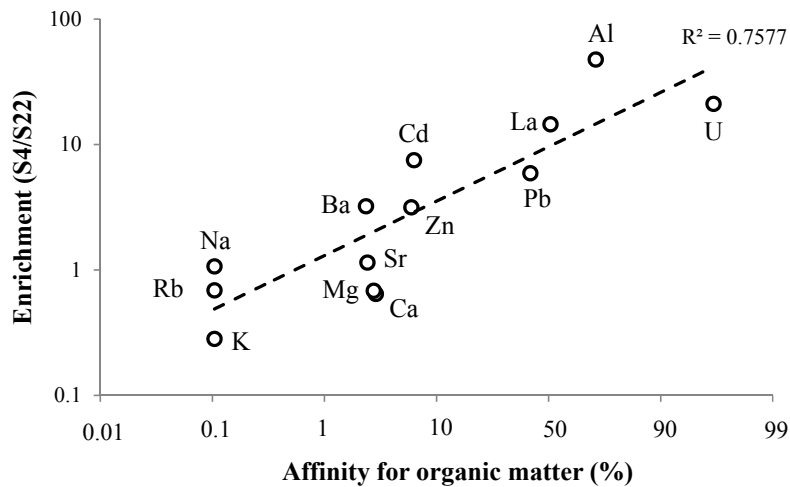
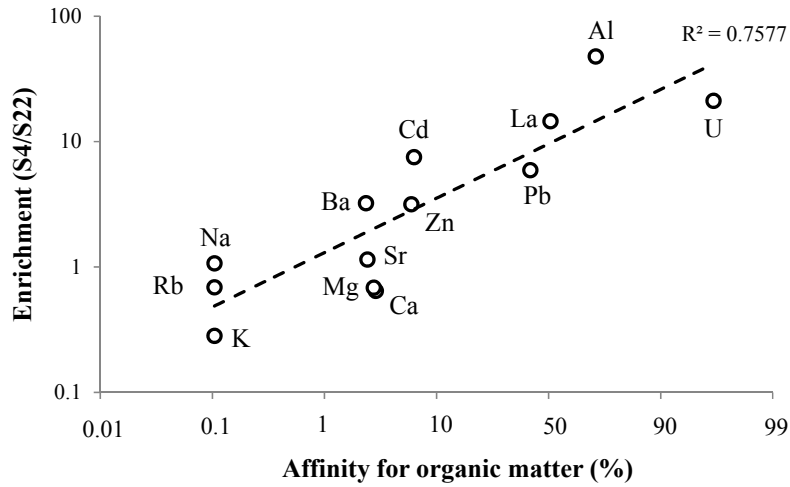
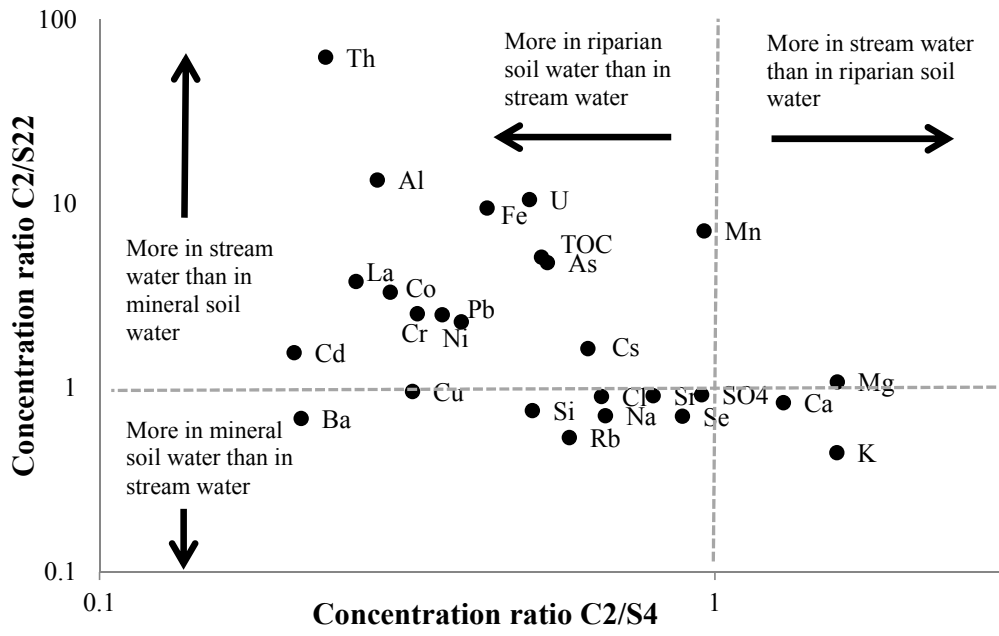


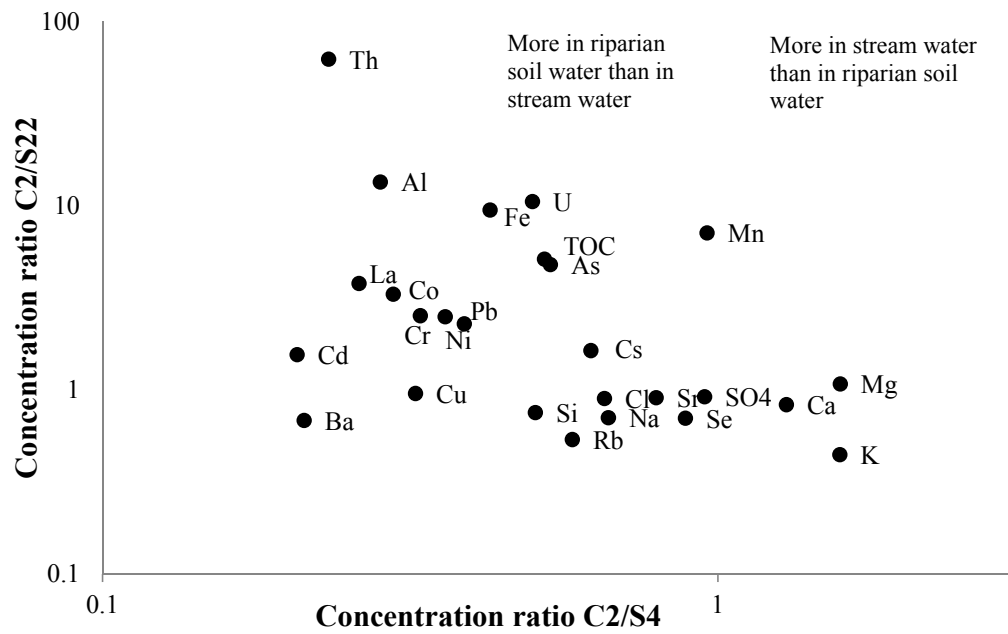
Figure 4. Relative enrichment in the riparian soil water and groundwater expressed as the ration between the average concentration in the riparian profile (S4) and the average concentration of the upslope podzol profile (S22). Elements marked in grey are included in the regression in Figure 5.



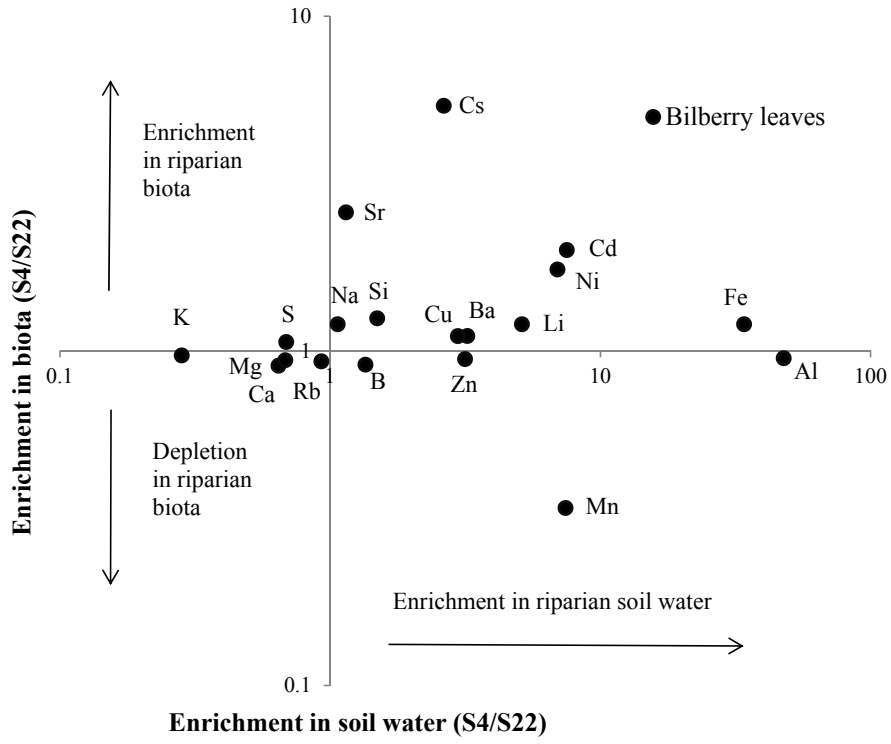
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Figure 5. Enrichment in average groundwater/soil water concentration when comparing the riparian zone (S4) and the upslope podzol (S22) as a function of the affinity for organic matter. The affinity for organic matter is plotted on a logit scale (Eq. 1).





5 Figure 6. Ratios between the average concentrations in stream water (C2) and riparian soil water (S4) (horizontal axis) and between the average concentrations in stream water (C2) and mineral soil water (S22) (vertical axis). Elements above the dashed horizontal line occur in higher concentrations in the stream water than in the mineral soil water. Elements to the left of the vertical lines occur in higher concentrations in the riparian soil water than in the stream water. The selection of elements is based on the available measurements in this study and the stream water data presented by Lidman et al. (2014).



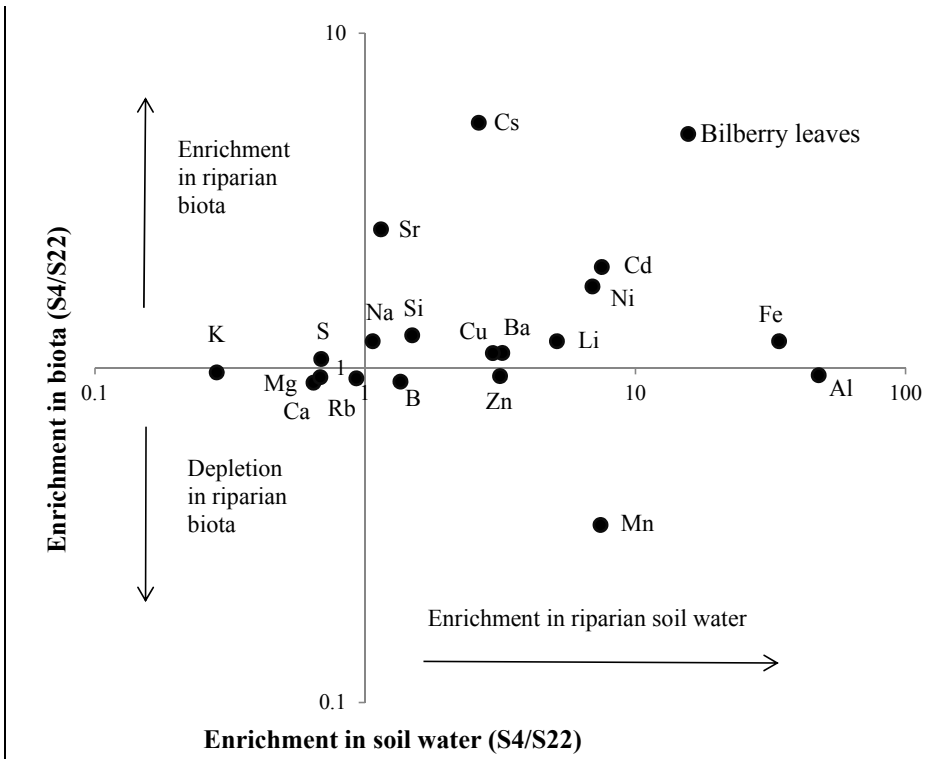


Figure 7. Enrichment of elements in bilberry leaves vs. enrichment in soil water when comparing the uphill site (S22) and the riparian site (S4).