

Interactive comment on “Chemical and U-Sr isotopic variations of stream and source waters at a small catchment scale (the Strengbach case; Vosges mountains; France)” by M. C. Pierret et al.

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Specific comments: 1) Abstract/introduction: although this study is intended to be a case study, the reviewer would like to see how the gained insights from this study help to understand the impact of such as vegetation cover and soils on evolution of surface waters at a small catchment scale and what are the global implications of these findings.

The vegetation cover and soils have a great influence on the chemistry of soil solutions. However, on the base of chemical mass balance this study show that the chemistry of

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the first meter soil solution didn't control strongly the signature of spring and stream waters at the catchment scale. Our study seems to show that the mineralogy, the secondary phases and the water pathways are the main factors explaining the signatures of stream waters. The global implications are that the water pathways and the secondary phases, especially clays have to be taken into account more deeply at the watershed scale. Despite the fact that soils and vegetation cover have a great influence on the water cycle balance (evapotranspiration, drainage, runoff. . .), the chemical compositions of waters are strongly modified by processes occurring within deep horizon along the specific water pathways.

2) Chemistry comparison of northern vs. southern slopes: in addition to the difference in mineralogy/hydrothermal alternation of the bedrock, the reviewer wonders whether the landscape positions (e.g., sun-facing vs. shade-facing) play a role in the soil development and water chemistry evolution. The effects of landscape aspect on microclimate conditions at the catchment scale have been commonly observed and may be relevant here. For example, it has been shown that for mid-latitude regions, different soil temperature and moisture content could be generated by aspect through controls on the amount of solar radiation at the catchment scale [e.g., Cooper, 1960, *Soil Sci.*, 90, 109–120; Churchill, 1982, *Earth Surf. Processes Landforms*, 7, 171–182.; Carter and Ciolkosz, 1991, *Geoderma*, 49, 199–213; Egli et al., 2007, *Clay Minerals*, 42, 373–398; 2010; *Geomorphology*, 114, 466–482.]

Line 25, p 3546 to line 4 p 3547 – has be change to:

In addition, the northern sun-facing slope is characterized by a drier and slightly warmer climate with 10% less precipitation than observed for the southern slope. The soils are brown acidic to ochreous brown podzolic and are generally about 1 meter thick. They are very coarse grained, sandy and rich in gravel (Fichter et al., 1998). The brown acidic soils are mainly located on the northern slope and are characterized by higher clay contents, lower K-feldspar, lower albite, higher cation exchange capacity (CEC), lower pH and lower organic matter content than the ochreous brown podzolic soils,

which are mainly located on the southern slope (Fichter 1997; Fichter et al., 1998). The pedological differences are due to the different mineralogical compositions of the northern and southern bedrocks, and the different types of vegetation but also the different orientations of the slopes. Indeed, exposure and consequently rainfall and temperature influence the chemical weathering of soils and organic matter, the soil acidity and processes of clay formation (Egli et al., 2007; 2010).

3) The reviewer would also like to see some saturation index (SI) values calculated based on the measured chemistry data of the streams and springs to back up the arguments of processes involved clay mineral precipitation/dissolution. Also, it may be necessary to present the mineralogy of the soils and bedrock and to compare/discuss with the SI values of the waters. The SI values may help to elucidate the water-rock interaction processes

Recent numerical modelings of superficial waters have shown that only primary mineral weathering is not able to explained the chemical signature of river waters. Thus, the role of secondary phases, especially dissolution/precipitation of clay minerals, on the chemical composition of soil solution and river water have been explored and proposed in several studies using thermodynamic approach (Price et al., 2005; Godd ris et al., 2006; Maher et al., 2009; Violette et al., 2010; Beaulieu et al., 2011). However, significant uncertainties affect the prediction of thermodynamic properties of clay minerals. ΔG° values are only available for ideal structures whereas clay minerals can present large quality variations in term of cristallinity or composition (Al, Fe contents). As an illustration, field smectites can be a complex mixing of ideal end-members as Ca-, Mg-, Na- or K-montmorillonites. In addition, several papers have highlighted the differences between thermodynamic and kinetic constants determined under experimental conditions with them in natural systems (White and Brantley, 1995; White and Brantley, 2003, Daval et al., 2011). That's why, the solubility products of clay minerals as montmorillonite or kaolinite have to be artificially increased (by a factor range from 8 to 15) to account for the Mg, Ca and aqueous silica concentrations in waters

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(Godderis et al., 2006; Violette et al., 2010; Beaulieu et al., 2011). Poorly crystallized clays have typically higher pK than theoretical idealized clays, and clays from recent soils or in active fractures are typically not perfectly crystallized. This was confirmed in the Strengbach case with SEM study of soils and rocks (not shown here). Furthermore, clay hydratation imply also variations of ΔH and then of pK_{eq} . So, considerable uncertainties surrounding the use of pK_{eq} for minerals like clays. In addition, during the water circulation through soils first and then more or less weathered and fractured bedrock, the saturation index in solution changes because the water becomes more concentrated and less acidic due to water/rock interactions. Then even when river water is oversaturated in respect to a mineral, the chemical elements in this water can come from the earlier dissolution of this same mineral. As suggested by the two reviewers, we calculated some saturation index in the different springs and stream of the Strengbach catchment (Figs. 1 and 2). The questions concerning mainly clays, we will discuss the saturation index of some of them: Ca-smectite, Mg-smectite (similar to Ca-smectite), Illite, kaolinite and chlorite. Using the theoretical pK_{eq} of ideal structures (see Godderis et al., 2006) we obtained that all the waters are oversaturated with respect to Ca- and Mg-smectite and illite. All spring except SH are oversaturated with respect to kaolinite. All springs are undersaturated with respect to chlorite. On the base of this first approach we can proposed that Mg in waters can be explained by a contribution of chlorite dissolution, which confirm the contribution of clay mineral dissolution in the chemical signatures of waters. However, smectite is an important component of the clay fraction from several weathering profiles at the Strengbach watershed whereas chlorite has been more rarely identified (Fichter et al., 1997; Prunier, 2008; Table 4). That's why the saturation index of Ca- and Mg-smectite have been calculated versus a large range of pK (figure below). Increasing the pK by a factor of 2 to 3 for the both smectite allowed to obtain $\text{Log}(Q/K) < 0$ for all springs (Fig. 1). Using the same factor imply that all the springs became undersaturated in respect to muscovite and illite. Then, this approach suggests that the contribution of clays can explained the chemical signature of Strengbach superficial waters. This is consistent with numerical model

studies proposing an increase of the solubility products of smectite to obtain a correct prediction of Si, Ca and Mg concentrations in waters (Godderis et al., 2006; Violette et al., 2010; Beaulieu et al., 2011). Thus, saturation index calculations, based on theoretical solubility products are probably not the best way to discuss the origin of chemical element in water. Finally, the Sr isotopic compositions and chemical signature of spring waters highlight the necessity to take into account the clay mineral as a source of element to explain the signature of waters (cf. figure 9 / this paper). Compared to these issues, we propose to not discuss these aspects of saturation index determination in the script because the document is already long. We added the reference Violette et al. (2010) that propose also the role of secondary minerals as clays (especially kaolinite and smectite) to explain the chemical composition of stream water in a watershed in India. Unfortunately, because of the large gap between theoretical and probably real saturation index values for clays the SI values will not really help to elucidate water/rock interactions processes. Ref : Daval D., Sissmann O., Menguy N., Saldi G.D., Martinez I., Corvisier J., Garcia B., Machouk I., Knauss K.G. and Hellmann R., 2011. Influence of amorphous silica layer formation on the dissolution rate of olivine at 90°C and elec-vated pCO₂. *Chemical Geology* 284, 193-209

Maier, K., Steefel, C.I., White, A.F., Stonestrom, D.A., 2009. The role of reaction affinity and secondary minerals in regulating chemical weathering rates at the Santa Cruz Soil Chronosequence, California. *Geochimica et Cosmochimica Acta* 73, 2804–2831

Price J.R., Velbel M.A. and Patino L.C., 2005. Rate and time scales of clay mineral formation by weathering in saprolitic regoliths of the southern Appalachians from geochemical mass balance. *Geol. Soc. Am. Bull.* 117, 783-794.

White, A.F., Brantley, S.L., 1995. Chemical weathering rates of silicate minerals: an overview. : *Chemical Weathering Rates of Silicate Minerals*, Vol. 31. Mineralogical Soc America, Washington, pp. 1-22

White, A.F., Brantley, S.L., 2003. The effect of time on the weathering of silicate min-

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erals: why do weathering rates differ in the laboratory and field? Chem. Geol. 202, 479–506

Violette A., Godderis Y., Maréchal J.C., Riotte J., Oliva P., Mohan Kuma M.S., Sekhar M. and Braun J.J., 2010. Modelling the chemical weathering fluxes at the watershed scale in the Tropics (Mule Hole, South India) : Relative contribution of the smectite/kaolinite assemblage versus primary minerals. Chemical Geology 277. 42-60.

4) The correlation presented in Figs. 4a and 4b, is somehow subjective. That's right because the correlations exist only for some springs. U and DOC are correlated for DOC-rich spring. But, DOC-poor spring can also have high U concentrations. As the speciation of U is not really a main subject here, we propose to skip all the discussion about relation between U, DOC and Fe concentrations. The speciation and behavior of U in springs, more or less concentrated in COD or more or less enriched in mineral or organic colloids can be a subject of another publication.

The information presented in Figs. 6 is not very clear. The objective of this figure is to show the lack of correlation between Sr isotopes and U AR. This lack implies that the U activity ratios are not linked to lithology or geographical location, in contrast to Sr isotopic signature. Therefore the U AR have to be explained by other processes than those explaining the Sr isotopes. That's why we have written in the legend: "In contrast to Sr isotopic compositions, the U AR of springs do not allow to distinguish between the northern and southern slopes".

Technical corrections: Page 3544 line 24-27: please be specific on how $^{234}\text{U}/^{238}\text{U}$ ratios changes along river flows and hydrological mixing. Text has been changed to : Consequently, $(^{234}\text{U}/^{238}\text{U})$ AR in superficial waters allow to identify river- flow patterns, and hydrological mixing by tracing the sources of water and recording mixing between superficial and groundwaters characterized by different U AR. Thus the $(^{234}\text{U}/^{238}\text{U})$ AR change along river flows and in function of hydrological mixing (e.g., Chabaux et al., 2001; Durand et al., 2005; Maher et al., 2006; Osmond and 1982;

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Paces et al., 2002; Riotte et Chabaux, 1999).

Page 3535 line 4-6: this sentence is not very clear to the reviewer. Supposedly p. 3545 Text has been changed to: The impact of physico-chemical processes in soil on the chemical balance of waters at the outlet is rather weak. For instance, the mean annual flux of Ca in soil solution at 60 cm depth represents 5 to 20% of the annual flux at the outlet, depending on the type of vegetation or soil (Cenki-Tok et al., 2009). Therefore, the chemical compositions of waters are mainly controlled by interactions occurring with the deep saprolite and bedrock rather than with soils.

Page 3535 line 15-18: again, this sentence is not clear to the reviewer, what are the controlling factors? Text has been changed to: The Sr signature at low discharge has been explained by important contributions of waters from the deep soil profile during the recession stage, whereas higher $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios at higher discharge are due to important contributions of waters from the saturated area of the catchment. Page 3545 line 26: 80 ha: please use SI units 80 ha was changed to 0,8 km² Page 3547 line 19-25: the description on spring locations is confusing: are CS3 and CS4 on southern side or northern side? The reviewer is right. Text is confusing because the waters of the 4 springs (CS1 to CS4), located on different slopes, finally arrived at the same place (a drinking water reservoir) where each of them has been collected. We therefore propose to simplify the description. The text has been changed to: The springs SG, ARG, RH, BH, CS3 and CS4 are located on the northern slope and the springs CS1, CS2, SH and RUZS emerge at the southern slope (Fig. 1). Page 3553 line 3-18: is the difference caused by different bedrock mineralogy (including different types of bedrock and hydrothermal alteration), or different degrees of water-rock interactions, or N. vs. S landscape locations? The paragraph mentioned by the reviewer concerns the explanation of chemical signature of SG spring, which is characterized by the highest Ca and Mg concentrations. The chemical differences among the different springs from the Strengbach watershed can be generally related to the different bedrock mineralogy, which is due to the fact that the granite from the northern slope

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has been stronger hydrothermally altered than that of the southern slope. In addition, the banded gneiss located at the top of the northern slope has a different mineralogy than the granites. The spring SG, emerging in the gneiss is a good illustration of the relation between lithology and geochemistry of water. SG is characterized by the highest Mg concentration linked with the gneiss mineralogy (more chlorite). In addition, among the springs circulating through a same lithology, the differences can be explained by intensity of water-rock interactions (recorded by pH, Alk or TDS). Text has been changed to: The geochemical signature of springs can generally be linked to specific lithological and mineralogical differences existing for the two hillsides of the Strengbach catchment. This is particularly obvious for the SG spring, which emerges near the top of the catchment, just under the banded gneiss, whereas the other sources emerge within the granitic environment (Fig. 1). Page 3554: line 26-27: the northern slope samples are more radiogenic?? Typo here? Text is confusing and has been changed to: The springs, bulk soils and clays from the southern slope show higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than those from the northern slope. Clay fraction contents in weathering profiles from northern slope are twice as big as those from the southern slope. This suggests that the impact of clay on the chemical composition of springs and streams is more important on the northern than the southern slope. This also explains why the springs from the northern slope are more radiogenic (Fig. 4a and b) with comparatively higher Mg/Ca and Mg/Sr ratios (Fig. 8a and b) than those from southern slope. Page 3556 line 18-21: it is not clear to the reviewer that why this argument is supportive or against that $U < 1$ ratios are or not derived from the weathering of soils? Please elaborate. The objective of this paragraph is to demonstrate that U coming from the upper soil horizons cannot explain the U AR in spring waters. We presented three arguments: 1) U mass balance calculation, 2) U concentration and 3) U AR. The text has been changed to: One might simply suggest that the U AR < 1 in the Strengbach source waters are the results of circulation through already weathered soils, supposedly having U AR < 1 due to previous weathering. However, chemical flux balance calculations show that the annual U fluxes from the soils under spruces or beech trees represent at maximum

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about 8% or 22%, respectively, of the annual U flux at the outlet (Table 3). At the same time, the U concentrations in the different springs can reach on average 0.345 ppb whereas they range only between 0.011 to 0.023 ppb (factor of 30 to 15 lower) in the deep soil solutions of the two experimental plots (Table 2). In addition, ($^{234}\text{U}/^{238}\text{U}$) AR determined on soil solutions from depths between 5 and 70 cm, range from 0.899 and 0.945 under spruces and from 0.953 to 1.194 under beech trees (Prunier, 2008) whereas they are significantly low for some spring waters (0.82). This indicates that circulations and interactions in the saprolite and bedrock (below the soil) control the U isotopic signature in spring and stream waters. Page 3558 line 21-24: SI values may reveal more information about the evolution of water chemistry here. The modeling of chemical composition of the waters from the Ringelbach catchment implies dissolution of primary minerals of granite and precipitation of secondary phases such as clays but no dissolution of clays (Schaffauser, 2013). For the same reasons than explained in question 3, we propose to avoid discussion on SI values in this paper. Ringelbach stream waters present higher alkalinity, pH and also conductivity, K, Mg, Si and Ca concentrations (not show) than spring and stream waters from Strengbach watershed, which is coherent with the fact that the U AR is correlated with intensity of weathering (Fig. 11). The log (Q/K) for Ringelbach waters with respect to Ca- or Mg-montmorillonite will be higher than those for Strengbach waters.

Page 3559 line 10-12: why smectite? What about the SI values for smectite in these waters. The high pH and alkalinity observed for the BH source are in this case consistent with the fact that its water has interacted with fresher bedrock; this further implies a stronger weathering intensity. In addition BH is characterized by high Mg and Si concentrations. Numerical modeling proposed that Si and Mg fluxes in superficial waters are explained by dissolution of Mg-smectite (Godderis et al., 2006; 2009; Violette et al., 2011). Thus, we proposed that BH is characterized by higher dissolution rate of smectite along the pathway of this source water. See also explanation to question N°3.

Page 3560 line 1-3: samples plotted in Fig 3 are not grouped with time, so it is hard

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to assess the temporal variations. The data obtained during 2 hydrological years allow for the analysis of the temporal variations of the springs (Fig. 3). The spring RUZS shows the largest variations, which can be explained by the fact that this spring, drains wetland (10 to 15% of the whole catchment area) with fluctuations in the groundwater level and contributions. The chemical concentrations of RUZS are given in table 1b and show the largest variations. In addition, in figure 3 the RUZS data (black circle with white ring) show the largest variations among the plotted data. It's not possible to group with time the data.

Page 3563: line 5 to 12: all of these factors are related to the parent material/bedrock mineralogy. They can be combined as in one factor rather than the three factors here. As proposed, we reduced the three first factors to one. The text has been changed to: This heterogeneity is mainly related to: - the parent material (gneiss, more or less hydrothermally altered granite) and the degree of their weathering. This is confirmed by the fact that the sources draining the northern slope (hydrothermally much more altered) have higher TDSw-, pH values, higher Ca, K, Mg concentrations and lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than sources draining the southern slope.

We propose a revised version, which takes account of the changes and responses to the two reviewers.

Please also note the supplement to this comment:

<http://www.hydrol-earth-syst-sci-discuss.net/11/C2638/2014/hessd-11-C2638-2014-supplement.pdf>

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., 11, 3541, 2014.

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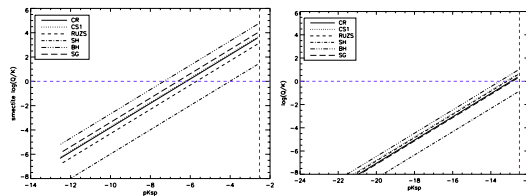


Fig. 1: Log (Q/K) vs different values of pK_{eq} for Ca-smectite (left) and illite (right) for several springs of the Strengbach watershed. The red line corresponds to the theoretical value for idealized structure. Godderis (pers. com.).

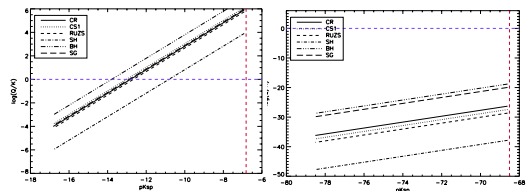


Fig. 2: Log (Q/K) vs different values of pK_{eq} for kaolinite (left) and chlorite (right) for several springs of the Strengbach watershed. The red line corresponds to the theoretical value for idealized structure. Godderis (pers. com.).

Fig. 1.

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The global implications are that the water pathways and the secondary phases, especially clays have to be taken into account more deeply at the watershed scale. Despite the fact that soils and vegetation cover have a great influence on the water cycle balance (evapotranspiration, drainage, runoff...), the chemical compositions of waters are strongly modified by processes occurring within deep horizon along the specific water pathways.

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Fig. 2.

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