AUTHORS REPLY TO REVIEWER 2 (Dr. M. Brenčič)

INTRODUCTION

We thank the reviewer for his thoughtful and thorough review. His open and constructive comments give us the opportunity to improve the paper in terms of completeness of data and results and to more substantially and evidently justify conclusions on the basis of the data presented (the lack of which, is the major negative comment of the reviewer).

On a general level, before providing specific replies to general and specific comments received by reviewer 2, we would like to pinpoint that some common assumptions regarding the hydrogeological behaviour of slopes in the Alps (for which reviewer 2 has a very detailed knowledge) are not always directly transferable to slopes of the northern Apennines, and to the Ca' Lita test site in particular. The reason for this, is that the hydro-geologic setting of the northern Apennines is largely dominated by low permeability formations, which in many cases are to be considered as aquicludes unless they are affected by regional tectonic features inducing significant secondary permeability (Gargini et al., 2008). Limestone-gypsum formations acting as aquifers, that are quite common in the Alps, are indeed quite sporadic in the northern Apennines and they are only present in the higher portion of the chain, far away from the analysed case study where, in turn, permeable hydrogeological units are constituted by fractured and faulted turbidites-like formations.

- Gargini, A., Vincenti, V., Piccinini, L., Zuppi, G.M. and Canuti, P. 2008: Groundwater flow systems in turbidites of the Northern Apennines (Italy): natural discharge and high speed railway tunnel drainage, Hydrogeol. J., 16 (8), 1577-1599.

REPLIES TO GENERAL COMMENTS TO THE PAPER

(comments by the reviewer are in BOLD-ITALIC)

1) Regional hydrogeological conditions are precisely described and illustrated by the sketches of regional and local geology. I will expect that also conceptual hydrogeological model will be presented. In their interpretation deep water flow plays important role but they do not illustrate how this water is rising up. For the interpretation it is important to propose flow along the fault (which of them is behaving as a conduction path) or through the whole mass of bedrock under the landslide.

Short reply:

We partially agree

Long reply:

Providing a through conceptual hydrogeological model of the northern Apennines was believed to be beyond the scope of the paper. Conceptual hydrogeological models of the northern Apennines are proposed in recent literature as cited in the paper (see for instance Gargini et al., 2008).

Regarding the key role of uprising flow along fault lines, we agree with the referee, as it is one of the core aspects of the explanation of the nature of groundwater in Ca' Lita and has been extensively investigated in literature.

On this respect, we'd like to pinpoint that the paper already includes several elements that evidence the role of a regional fault striking NW-SE as the preferential path for deep groundwater uprise in Ca' Lita. For instance, the cross section in Fig. 1B shows that the above mentioned regional fault cuts through the bedrock and intercepts the landslide. Moreover, Fig. 2A shows that a zone of high tectonic fracturing due to the fault line affects the entire bedrock underneath the landslide.

Intended consequent amendments to the paper:

- ✓ We will make more explicit reference to the conceptual hydrogeological model presented by Gargini et al., 2008.
- ✓ In Fig. 1A, we will highlight the trace of the NW-SE strike fault line crossing the Ca' Lita landslide area and will provide the following references for its description:
- ✓ We will stress the key role of fault lines in determining the uprise of deep groundwater in the northern Apennines, also by integrating references with the following works:

Cited references:

- Gargini, A., Vincenti, V., Piccinini, L., Zuppi, G.M. and Canuti, P. 2008: Groundwater flow systems in turbidites of the Northern Apennines (Italy): natural discharge and high speed railway tunnel drainage, Hydrogeol. J., 16 (8), 1577-1599.
- Minissale, A., Magro G., Martinelli G., Vaselli O. and Tassi, F. 2000: Fluid geochemical transect in the Northern Apennines (central-northern Italy): fluid genesis and migration and tectonic implications, Tectonophysics 319(3), 199-222)
- o Conti, A., Sacchi, E., Chiarle, M., Martinelli, G. and Zuppi, G.M. 2000: Geochemistry of the formation waters in the Po plain (Northern Italy), Appl. Geochem., 15 (1), 51-65. Ghisetti, F., Kirschner, D., and Vezzani, L.: Tectonic controls on large-scale fluid circulation in the Apennines (Italy), Journal of Geochemical Exploration, 69–70, 533-537, 2000.
- Capozzi, R. and Picotti, V.: Fluid migration and origin of a mud volcano in the Northern Apennines (Italy): role of deeply rooted normal fault, Terra Nova, 14 (5), 363-370, 2002.
- Capozzi, R. and Picotti, V. : Spontaneous fluid emission in the Northern Apennines: geochemistry, structures, and implications for the petroleum system, Geological Society Special Pubblications, 348, 115-135, 2010.
- Martinelli, G., Cremonini, S., and Samonati, E.: Geological and Geochemical Setting of Natural Hydrocarbon Emissions in Italy, Advances in Natural Gas Technology, 79-120, 2011,
- Bettelli, G., Panini, F., and Capitani, M.: Carta geologico-strutturale dell'Appennino emiliano sudorientale, Bologna, Atti Terzo Seminario sulla Cartografia Geologica Bologna, Stampa Labanti, 2002.
- Vannucchi, P., and Bettelli, G.: Myths and recent progress regarding the Argille Scagliose, Northern Apennines, Italy, International Geology Review, 52, 10-12, 1106-1137, 2010.

2) For a reader not knowing local information there is also scarcity of information about landslide geometry. Information about the area, width, slope and aspect must be added at the beginning.

Short reply:

We agree

Long reply:

In the submitted paper, we deliberately reduced the number of information given at the beginning in order to make it more concise. Actually, such information can be found in different sections of the paper.

Intended consequent amendments to the paper:

- ✓ We will concentrate all requested information about landslide geometry in the initial section.
- ✓ We will also add further information about landslide body and bedrock permeability deriving from in-situ tests included in some of our previously published papers (see Ronchetti et al., 2009) so to provide a full hydrogeological characterization framework.

Cited references:

- Ronchetti, F., Borgatti, L., Cervi, F., Gorgoni, C., Piccinini, L., Vincenzi, V., and Corsini, A.: Groundwater processes in a complex landslide, northern Apennines, Italy, Nat. Hazards 5 Earth Syst. Sci., 9, 895–904, doi:10.5194/nhess-9-895-2009, 2009.

3) I would also expect more easily scanned water balance of the landslide. I suggest representing water balance concept with the system of equations that are easily readable than plain text description.

Short reply:

We agree

Long reply:

The reviewer provides a constructive comment.

Intended consequent amendments to the paper:

- ✓ We will include in section 7 (discussion) balance equations.

4) However, based on the number of the analyses my opinion is that number of samples is too few to justify such strong conclusions as it is deep groundwater flow. In the area where they are working strong seasonality effects can be present in isotopic and chemical composition of water cycle. Only with few samples it is difficult to reliably interpret such influences. I suggest using multiple hypotheses approach.

Short reply:

We do not agree with the fact that there are too few analyses and we stand with our interpretation, but will improve and extend our arguments.

Long reply:

For this study, 22 δ18O isotopic analyses have been carried out, 19 of which have been coupled with δ2H . Moreover, 12 chemical analyses have been performed and they included main and trace ions.

All the water sampled originate from groundwater (drains, springs and piezometers) with depths greater than 10 meters. No shallow groundwater was sampled, as evaporation processes could be active at the surface, especially during the summer periods. In particular, the more representative samples concern the deepest drainage system (DrA), which collects water from a depth of more than 50 meters.

Furthermore, the sampling campaigns spread out over 5 consecutive years and involved warm and cold seasons.

Isotopical and chemical data resulting from analyses of that large amount of samples are consistent with data available in Bibliography (Conti et. al., 2000; Minissale et al., 2000; Duchi et al., 2005; Boschetti et al., 2010 and references therein) for this part of the Apennine chain, and they all point to the presence of an external deep fluid influencing the normal snow-melt/rainfall recharge in the groundwater of Ca’ Lita.

In the northern Apennines, groundwater recharged by rainfall and snow-melt, never show annual δ18O values lower than -6‰ (see for instance values reported in Minissale et al., 2000 and Iacumin et al., 2009). Only in the case of non-meteoric groundwater recharge, such as in correspondence of geothermal fields, mud cones and/or cold springs, δ18O values can be less negative (Minissale et al. 2000; Minissale and Vaselli, 2011) and be similar to these of Ca' Lita (that are about -5‰ in DrA)

The groundwater sampled in the deepest drain in Ca' Lita (DrA) is strongly enriched in Na+-SO42--Cl- ions. As the two geological formations are mainly composed by clays and silicates (as reported in Section 5.5) this chemical composition of groundwater cannot be explained by the simple interaction between rainfall/snowmelt and bedrock or slope deposits.

This is also proven by the results of Leaching tests and Phreeqc simulations reported in the paper (Section 5.4 and 5.5). Leaching tests were conducted using several samples of the two geological formations outcropping in the Ca’ Lita area. As specified in the paper, samples were collected at the Ca' Lita site as well as in other areas of the Apennine, so to provide a very representative picture of possible variability in mineralogy. Phreeqc was used to verify the final chemical composition reached by the water after an equilibrium-approach interaction with the mineralogy detected on the basis of diffractometry analysis of several samples.

In particular, leaching tests and Phreeqc simulations pointed out that soils couldn't release Cl-, even if the interaction is pushed to the equilibrium. The same can be observed for the B- content. This behaviour can be easily explained taking into account the mineralogical phases which make-up the Ca' Lita slope: they cannot provide such ions. No Cl-phase such as halite is available in the slope, and evaporites-TUG deposits are located 10 km depth (as reported in section Fig 1b.) Groundwater interacting with sedimentary rocks (carbonate or siliceous) are characterized by B- contents lower than 1 mgl-1 (Mather and Porteous, 2001; Toscani et al., 2001). In more detail, only in vulcanic areas of the southern Tuscany, higher B- amounts (peaks up to 6.6 mgl-1) can be released by the rock (Bianchini et al., 2005) while evaporite rocks outcropping in northern Apennines could provide B in the range of 1-3 mgl-1.

Conversely, it would be very difficult to explain the high values of electric conductivity of groundwater (more than 6000 µScm-1) without assuming deep groundwater inflow. Normal groundwater electric conductivity in similar geological settings of the northern Apennines slopes is in the range of 100-1000 µScm-1 (Toscani et al. 2001). As a matter of fact, no evaporite formation that might locally enhance conductivity outcrops close to the site, so this cannot be an explanation for conductivity anomaly.

Intended consequent amendments to the paper:

- ✓ Improve text by including part of the above mentioned counter-deductions and references

Cited references:

- Mather, J., and Porteous, N.C.: The geochemistry of boron and its isotopes in groundwaters from marine and non-marine sandstone aquifers, Applied Geochemistry, 16(7-8), 821-834, 2001.
- Toscani, L., Venturelli, G. and Boschetti, T.: Sulphide-bearing Waters in Northern Apennines, Italy: General Features and Water-rock Interaction, Aquat. Geochem., 7 (3), 195-216, 2001.
- Bianchini, G., Pennisi, M., Cioni, R., Muti, A., Cerbai, N., and Kloppmann, W. : Hydrochemistry of the high-boron groundwaters of the Cornia aquifer (Tuscany, Italy), Geothermics, 34(3), 297-319, doi:10.1016/j.geothermics.2005.04.002, 2005.
- Minissale, A., and Vaselli, O.: Karst springs as “natural” pluviometers: Constraints on the isotopic composition of rainfall in the Apennines of central Italy, Applied Geochemistry, 26(5), 838-852, 2011.
- Iacumin P., Venturelli, G., and Selmo, E.: Isotopic features of rivers and groundwater of the Parma Province (Northern Italy) and their relationships with precipitation, J. Geochem. Explor., 102 (2), 56-62, 2009.
- Minissale, A., and Vaselli, O.: Karst springs as “natural” pluviometers: Constraints on the isotopic composition of rainfall in the Apennines of central Italy, Applied Geochemistry, 26(5), 838-852, 2011.
- Boschetti, T., Toscani L., Shouakar-Stash O., Iacumin P., Venturelli G., Mucchino C., and Frape, S.K.: Salt Waters of the Northern Apennine Foredeep Basin (Italy): Origin and Evolution, Aquat. Geochem., 17(1), 71-108, 2010.
- Minissale, A., Magro G., Martinelli G., Vaselli O. and Tassi, F.: Fluid geochemical transect in the Northern Apennines (central-northern Italy): fluid genesis and migration and tectonic implications, Tectonophysics 319(3), 199-222, 2000.
- Duchi, V., Venturelli, G., Boccasavia, I., Bonicolini, F., Ferrari, C. and Poli, D. Studio geochimico dei fluidi dell’Appennino Tosco-Emiliano-Romagnolo, Boll. Soc. Geol. It., 124, 475–491, 2005.
- Conti, A., Sacchi, E., Chiarle, M., Martinelli, G. and Zuppi, G.M.: Geochemistry of the formation waters in the Po plain (Northern Italy), Appl. Geochem., 15 (1), 51-65, 2000.

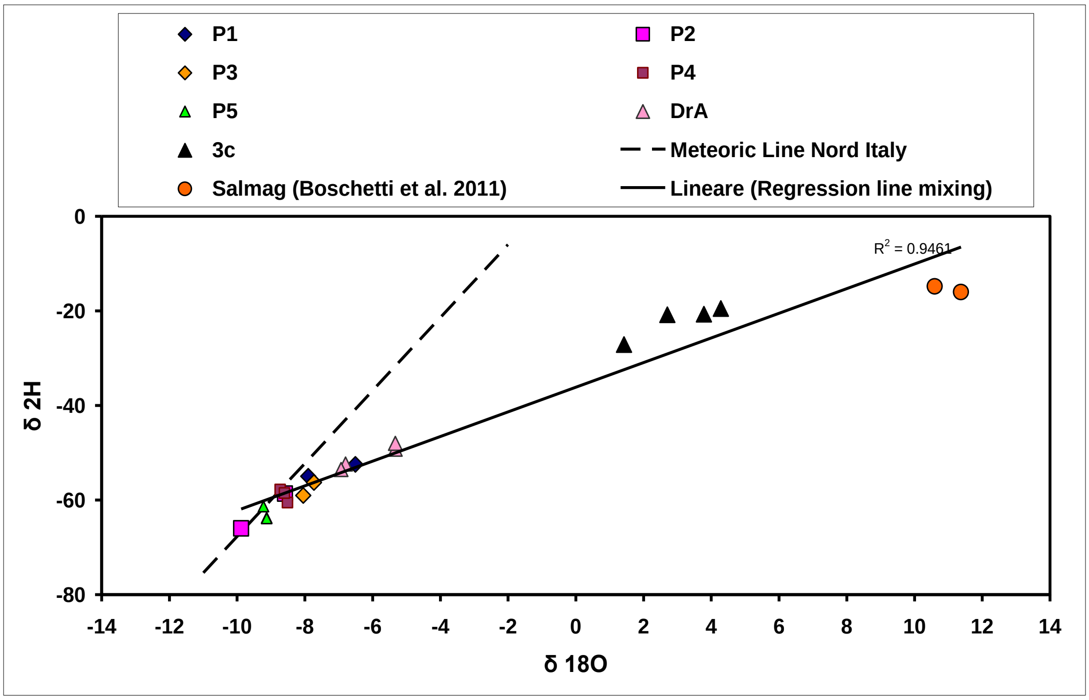
5) In chapter 5.3. Groundwater isotopic analyses authors discuss results of isotope analyses. Based on the reported results I can only partly agree with their interpretation. Their data are nicely represented in the Fig. 6. Large part of the samples is positioned below the regional (Italian) meteoritic water line - RMWL. However, it is interesting that they are positioned on the same line with lesser slope than RMWL. This is typical situation of the evaporation effect. Probably such isotopic composition can be also related to the presence of connate waters in evaporates. However, such deviation from RMWL can be also the consequence of exchange of HCO3- but due to the fact that partial pressures of CO2 in the groundwater and soil at the site are rather low such mechanism is very unlikely. Authors should consult some of the classical text books of isotope geochemistry (e.g. Gat, Mook, Fritz & Fontes, Clark & Fritz, IAEA etc.). Effect of evaporation line presence must be explained and used in the interpretation of the results.

Short reply:
We stand with our interpretation of the groundwater isotope data but will improve and extend our arguments and discuss the points raised by the reviewer.

Long reply:
In DrA, that is the deepest drainage system (depth between 50 and 100 m and a mean discharge of a few l/m), the stable isotopes are generally enriched and their values vary with a range of -1.6‰ δ18O and of -4.31‰ δ2H. The samples have been collected for several years during different seasons.
This variation in the isotopic data is, in our interpretation, due to a mixing between groundwater (which is recharged by local rainfall/snowmelt) and deep groundwater (connate water or oil field water).
We believe that this cannot be the effect of evaporation, as this process can only occur if groundwater table is close to the surface (where heating of the soils can be active) or some ponds directly connected with the groundwater can allow evaporation (Mazor, 1997; Kendall and Mc Donnell, 1998). This is certainly not the case in Ca' Lita: groundwater is located at depths greater than those suffering from temperature variations (groundwater temperature have been monitored in several boreholes and remained constant at 13.5°C) and summer rainfall cannot infiltrate through the soil, as clearly demonstrated by applying the Thornthwaite and Mater (1957) soil-balance equation.
Connate water or oil field water?
Given that the connate waters in northern Apennines are located in the frontal part of the chain (see QM in Fig.1a,b of our manuscript; reference: Bonini, 2007), more than 15 km north from Ca’ Lita, we can exclude the presence of connate water in the Ca’ Lita site (the absence of QM close to Ca' Lita is evident also in the geological cross-section in Fig. 1b). Instead, the widespread presence of oil field water in LU (Fig. 1a,b in our manuscript) is reported by several authors (such as: Buttinelli et al., 2011 and reference therein, Capozzi and Picotti,2010; VIDEPI project).
The mixing hypothesis is supported by the perfect alignment that exists in a δ18O -δ2H plot (plot below) between the Ca’ Lita groundwater and the oil field water of the northern Apennines. Using the same graph, this mixing effect has been documented and proven by other authors in northern Apennines as well (Capozzi and Picotti, 2002).

To further argument this fact, the following δ18O -δ2H plot (which is similar to the plot in Fig. 6) includes also the isotopic values measured in Salsomaggiore well in Parma Province (data points labelled as "Salmag" from Boschetti et al. 2010). This well pumps oil and gas from sandstone formation (TU as described in the geological section) at a depth of more than 3000 m. Moreover, the dots labelled as "3c" refer to the Regnano Mud Cone where a deep well extracts oil and gas from a depth of around 2000 m (Capozzi e Picotti 2002). The mixing line that connect the groundwater samples with the oil field isotopic data (Ca'Lita, Regnano, Salsomaggiore) reported in the plot has a R2 of 0.95. Taking into account the only DrA samples, the regression line can be expressed by the following equation: δ2H= 2.6*δ18O – 35 (R2=0.95).

As reported by Kendall and Caldwell (1998), the slope of the evaporation regression line ranges between 3.9 (humidity equals to 0%) and 6.8 (humidity of 95%). Celico (1988) provided for the Italian area a slightly more restricted range, included between 4 and 6 (with the higher values more common for the northern Italy). In our case, the gradient is considerably lower in both cases (equal to 2.6). In addition to that, it should be noticed that DrA is characterized by the simultaneous presence of conductivity and δ18O values for three different sampling campaigns (see B-D-F in Tab.3 of our manuscript). As reported by Gonfiantini et al. (1974) and Simpson et al. (1987) evaporation process leads to positive correlation between salinity and δ18O in the residual water. In our case, we found that the samples that showed the most enriched values of δ18O are characterized by lower conductivities and this fact cannot be physically explained as a result of evaporation.



Moreover, there is ample geochemical evidence for the mixing effect just by considering the high content of ions B-Cl-. As discussed in more detail at points 4 and 10, their abundance cannot be explained by evaporation processes in the unsaturated zone. Nor it can be explained by local geology, as there are no mineralogical phases containing Cl- and B-. Moreover, possible B-rich water adsorbed in clay minerals cannot be released by exchange processes at low temperature (see the more detailed reply in point 12).

It should also be pinpointed that all the shallow springs, in similar geological context as Ca' Lita, are characterized by a Ca-HCO3 water type and B- is lower than 1 mgl-1 (Toscani et al., 2001).

Intended consequent amendments to the paper:

- ✓ Improve text by including part of the above mentioned counter-deductions and references.
- ✓ Include the plots shown above.

Cited references:

- Bonini, M.: Interrelations of mud volcanism, fluid venting, and thrust-anticline folding: examples from the external northern Apennines (Emilia-Romagna, Italy), J. Geophys. Res., 112, 1–21, 25, 2007.
- Boschetti, T., Toscani L., Shouakar-Stash O., Iacumin P., Venturelli G., Mucchino C., and Frape, S.K.: Salt Waters of the Northern Apennine Foredeep Basin (Italy): Origin and Evolution, Aquat. Geochem., 17(1), 71-108, 2010.
- Buttinelli, M., Procesi M., Cantucci B., Quattrocchi F., and Boschi E.: The geo-database of caprock quality and deep saline aquifers distribution for geological storage of CO2 in Italy, Energy, 36, 2968-2983, 2011.
- Capozzi, R. and Picotti, V.: Fluid migration and origin of a mud volcano in the Northern Apennines (Italy): role of deeply rooted normal fault, Terra Nova, 14 (5), 363-370, 2002.
- Capozzi, R. and Picotti, V.: Spontaneous fluid emission in the northern Apennines: geochemistry, structures, and implications for the petroleum system, Geol. Soc. Spec. Publ., 348, 115–135, 2010.
- Toscani, L., Venturelli, G. and Boschetti, T.: Sulphide-bearing Waters in Northern Apennines, Italy: General Features and Water-rock Interaction, Aquat. Geochem., 7 (3), 195-216, 2001.
- Thornthwaite, C. W. and Mather, J. R.: Instruction and tables for computing potential evapotraspiration and the water balance, Publ. Clim. Drexel Inst. Technol., 10, 185–311, 1957.
- Boschetti, T., Toscani L., Shouakar-Stash O., Iacumin P., Venturelli G., Mucchino C., and Frape, S.K.: Salt Waters of the Northern Apennine Foredeep Basin (Italy): Origin and Evolution, Aquat. Geochem., 17(1), 71-108, 2010.
- Kendall, C., and McDonnell, J.J.; Isotope tracers in Catchment Hydrology, Elsevier Sciences., Amsterdam, 839 pp., 1998.
- Kendall, C., and Caldwell, E. A.: "Fundamentals of Isotope Geochemistry", In: C. Kendall and J.J. McDonnell (Eds.), Isotope Tracers in Catchment Hydrology, Elsevier Science, Amsterdam, pp. 51-86, 1998.
- Mazor, E.: Chemical and Isotopic Groundwater Hydrology, Marcel Dekker Inc., New York, 413 pp., 1997.
- Celico, P.: Prospezioni idrogeologiche, Vol. I. Pitagora, Napoli, Italy, 735 pp, 1986.
- Gonfiantini, R., Dincer, T., and Derekoy, A.M.: Environmental isotope hydrology in the Honda region, Algeria, Isotope Techniques in Groundwater Hydrology, IAEA, Vienna,1, 293-316, 1974.
- Simpson. H.J., Hamza, M.S., White, J.W.C., Nada, A., and Awad, M.A.: Evaporative enrichment of deuterium and 18O in arid zone irrigation, Isotopes techniques in Water Resources Development, IAEA Symposium, 299, Vienna, 241-256.

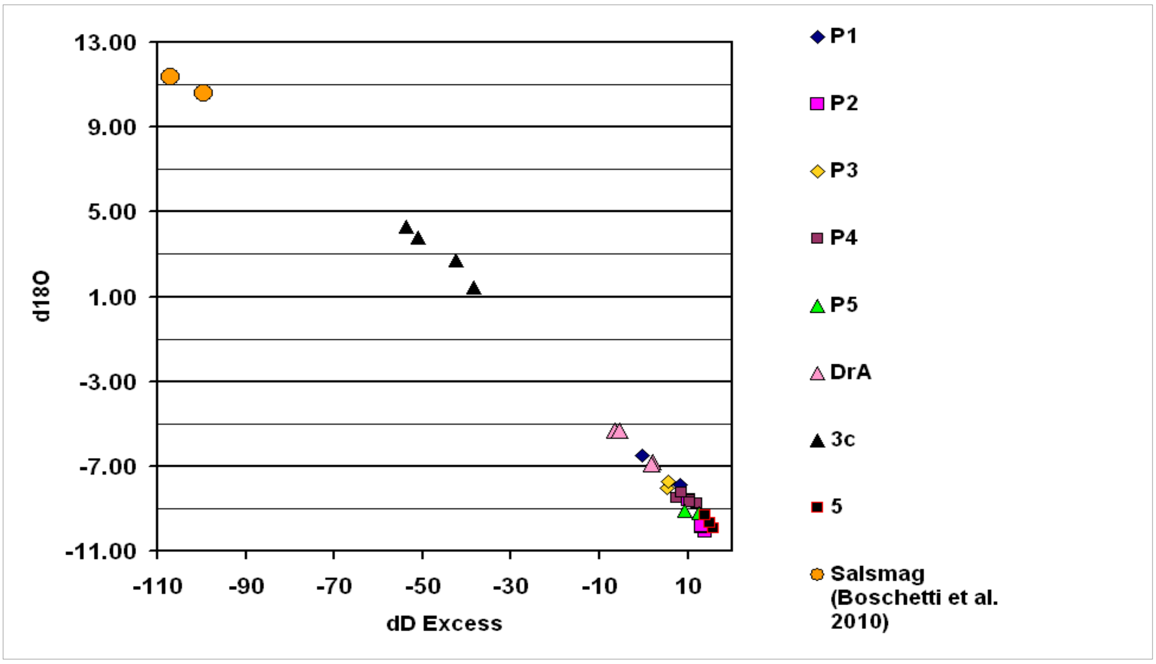
6) It will be also very helpful if they can use deuterium excess approach which can help a lot in the interpretation of isotope data.

Short reply:

We agree

Long reply:

As suggested by the referee, we have analyzed the deuterium excess (d) that has been calculated as d=δ2H -8*δ18O. Results are plotted with δ18O in the graph below, legend is referred to the graph that has been previously discussed at point 5. Once again, values from Ca' Lita are in line with typical values for mud-volcanoes (dots labelled as "3c" refer to the Regnano mud cone, data from Capozzi e Picotti, 2002) , and specifically with values from oil-fields like SalsoMaggiore (data points labelled as "Salmag" from Boschetti et al. 2010).



Intended consequent amendments to the paper:

- ✓ We will include local available deuterium excess data
- ✓ We will include local available δ18O - d plot and discuss it.

Cited references:

- Capozzi, R. and Picotti, V.: Fluid migration and origin of a mud volcano in the Northern Apennines (Italy): role of deeply rooted normal fault, Terra Nova, 14 (5), 363-370, 2002.
- Boschetti, T., Toscani L., Shouakar-Stash O., Iacumin P., Venturelli G., Mucchino C., and Frape, S.K.: Salt Waters of the Northern Apennine Foredeep Basin (Italy): Origin and Evolution, Aquat. Geochem., 17(1), 71-108, 2010.

7) For reported study I will expected some information on the isotope altitude effect which can help to discern recharge area of the water. There is no such information in the paper. Authors should stick more to the local information about isotopes in water than to regional interpretation of Longinelli and Selmo, 2003 that represent statistical (averaging) interpretation from data originating from earlier times than results representing in the paper. Authors should try to obtain results of precipitation sampling from some of the near station in the GNIP network of IAEA. Based on these data they should interpret what are expected fluctuations of isotopic composition in precipitation and consequently in local groundwater. If possible from these data they should try to estimate also altitude effect that can help to understand recharge area.

Short reply:
We agree in principle, but unfortunately GNIP data are not of much help for a number of reasons.

Long reply:
This answer is also connected to the answer to point 5.
We agree in principle with the referee that clear information about isotope altitude effect can help the reader. Following his suggestion we made a further and more comprehensive literature research on the isotopic values characterizing rainfalls in the study area.
In particular, as suggested by the referee, we started focusing on the GNIP-IAEA rain-gauges network. It includes 2 stations that are located quite close to the landslide's site:
1) S. Pellegrino Alpe station (altitude 1520 m a.s.l.), Record is not continuous. Sampling started from 1993 to 2002, data (δ 18O : max -2.42‰; min -14.30‰; weighted mean -7.61‰) have been collected monthly. About 30 km south-west of Ca' Lita.
2) Bologna station (altitude 35 m a.s.l.). Record is not continuous, Sampling started from 1996 to 2000, data (δ 18O : max -2.87‰; minx -13.66‰; weighted mean -7.69‰) have been collected monthly. Approximately 50 km north-east of Ca' Lita.
Despite the 1500 metres of altitude difference, mean annual values of δ18O are similar and they don't show, for these time-windows, an altitude effect. Anyway, as correctly evidenced by the Reviewer, Longinelli and Selmo (2003) assessed the altitude effect as about -0.2‰ δ18O/100 m for the entire Italian peninsula. By analysing further isotopic data in rain-gauge stations located in northern Italy, Longinelli et al. (2006) pointed out that warmest sampling periods and so changes in atmospheric regime (such as 2003) could modify and so strongly reduce the isotopic gradient.
Recently, Cremaschi (2008) collected and discussed an huge amount of isotopic data δ18O-δ2H from shallow springs in the Secchia catchment. He concluded that, during the years 2006-2007-2008, this sector of northern Apennines was characterized by an average isotopic gradient of -0.1‰ δ 18O/100 m.
Longinelli et al. (2006) provided further details: mean annual δ 18O along the Po plain -is around -7‰ - - 8‰ (34 m a.s.l.) while it can increase to -10‰ near the highest relief (about 2100 m a.s.l.). From these data, Ca' Lita (max elevation of about 650 m) is expected to show a mean annual value of δ18O in the range of about -8‰ - -9‰. This data have been substantially confirmed by several springs flowing out from flysch rock

masses around Ca' Lita (see group labelled as 5 in Tab.3 of our manuscript: Pavullo, 715 m a.s.l.; Lusino, 441 ; Serramazzoni, 730; Nismozza, 1200) .

It should also be considered that DrA is characterized by δ18O = -5.33‰, while mean annual values greater than -6‰ are not detected in any rain-gauge of the network. As reported by the GNIP-IAEA records above, the more positive values are related to the isotopically heaviest rainfalls, which are concentrated during summer months. However, as demonstrate by applying the Thornthwaite and Mather (1957) soil balance formula at the case of Ca' Lita (see the manuscript), this summer precipitation aliquot cannot infiltrate through the soil (and, therefore, reach the aquifer) due to the high evapotraspiration.

In any case, even if we would assume that summer rainfalls can infiltrate, it would represent a small volume of water compared to that infiltrated during the more humid months and it would be mixed to the entire volume of water stored in the aquifer. Precipitations falling down in autumn, winter and spring show more negative δ 18O values and take an active part in feeding aquifers. This phenomenon has been documented by Iacumin et al. (2009) for wells, springs and a river in northern Apennines, reporting the following δ 18O values:

- Rivers: observation period from 2004 to 2006, samples were collected monthly. min. -9.8‰ (winter); max. -6.8‰ (summer).
- Groundwater: observation period from 2003 to 2005, samples were collected monthly. min. -8.0‰ max. -8.7‰

As clearly pointed out by Iacumin et al. (2009), springs and wells provide smoothed records of δ 18O compared to the analysed river and their isotopic values are shifted towards more negative values. That is due to a homogenization effect made by the flysch aquifers on the isotopic signal of rainfalls, together with the inability of the summer rainfalls to reach the groundwater.

The same results have been reported for central Italy by Minissale and Vaselli (2011). Authors conclude that springs can be used to provide a mean annual isotopic value of recharge.

In substance, since we are working at the hydrologic-year scale in a low-permeable aquifer, groundwater sampled in piezometers can be used for identifying the mean annual isotopic value of recharge. This gives the advantage of not having to deal with anomalous summer values. Among the others, P5 was characterized by the more negative and more constant in time values of δ18O (min:-9.22‰; max:-9.13‰) and it was selected as representative of the groundwater recharge. This value is similar to those found in springs flowing out from flysch rock masses around Ca' Lita (see springs labelled as 5 in Tab. 3)

<u>Intended consequent amendments to the paper:</u>

- ✓ Improve text by including part of the above mentioned counter-deductions and references.

<u>Cited references:</u>

- Longinelli, A., and Selmo, E.: Isotopic composition of precipitation in Italy: a first overall map, J. Hydrol., 270, 75–88, 2003.
- Longinelli, A., Anglesio, E., Flora, O., Iacumin, P., and Selmo, E.: Isotopic composition of precipitation in Northern Italy: Reverse effect of anomalous climatic events, Journal of Hydrology, 329(3-4), 471-476, 2006.

- Iacumin P., Venturelli, G., and Selmo, E.: Isotopic features of rivers and groundwater of the Parma Province (Northern Italy) and their relationships with precipitation, J. Geochem. Explor., 102 (2), 56-62, 2009.
- Minissale, A., and Vaselli, O.: Karst springs as “natural” pluviometers: Constraints on the isotopic composition of rainfall in the Apennines of central Italy, Applied Geochemistry, 26(5), 838-852, 2011.
- Cremaschi, F.: Evidenze isotopiche, chimico-fisiche e piezometriche della circolazione idrica sotterranea in acquiferi fratturati e porosi dell'Appennino settentrionale (Monte Modino, Alta Val Secchia) (Isotopical, chemical and piezometric evidences of groundwater circulation through fractured and porous aquifers of the northern Apennines), BSc Thesis, Università di Modena e Reggio Emilia, Italy, 115 pp., 2008.

8) Seasonality effect is probably present. From the Table 3 follows that range in DrA sampling point of _18O is 1,6‰ and for _2H is 5,6‰ that are rather high amplitudes. This can be the consequence of different end members mixing, however if such changes exist than landslide body is relatively highly permeable.

Short reply:
We do not agree

Long reply:
As explained in points 5 and 7, we exclude an evaporation effect.
Moreover we highlight that the deepest drain (DrA) was sampled in winter and in summer and in both periods the isotopic values were the same.
In the slope, the mean hydraulic conductivity is around 10-7 m/s, with in some areas values ranging up to 10-6 m/s (Ronchetti et al., 2009 and unpublished data).

Intended consequent amendments to the paper:
✓ include in text part of the above mentioned counter-deductions and references.

9) Authors also reporting tritium concentration that are not reported in the tables and they are not referenced. Data must be properly reference and analytical methods described in the chapter related to the isotopic methods. With the interpretation of tritium data one should be very careful, especially if only few data are available. In recent precipitation values bellow 5 T.U. are more probable than higher and concentrations around 10 T.U. are likely to coming from groundwater ages between 10 and 20 years, depending on the local conditions.

Short reply:
We partially agree

Long reply:

The T.U. = 10 has been used as marker for rainfalls in the Ca' Lita area, with specific reference to the hydrologic year 2009. This value was specifically obtained by averaging a complete annual record (2009) of three-monthly tritium data coming from the Secchia catchment (the same of Ca’ Lita). As cited in the Methods section of our manuscript, these data were published as a report by the Environmental Agency of Emilia Romagna Region (ARPA). In more detail, data from ARPA were collected from a shallow well (depth of 20 m), located about 10 km north of Ca' Lita , which intercepts an unconfined aquifer made up of highly-permeability gravel close to the Secchia riverbed (30 m far). On the basis of continuous chemical, isotopic and groundwater level monitoring, ARPA report concluded that this well is directly fed by the river, which in turn is directly linked to precipitation regime (as the catchment is mainly composed by low-storage formations). As a consequence, ARPA considered such sampling borehole as an isotopic marker of rainfall. For the specified 2008-2009 time-window, tritium values remained very close to 10 T.U. (more accurately: 9.8 T.U.).

Anyway, as suggested by the reviewer at point 7, we decided to check also the tritium values contained in the GNIP-IAEA database for the rain-gauges of the network that are closer to Ca' Lita. Unfortunately, tritium data are available only until 1995. Nevertheless, we still decided to make a comparison by using the 1994-1995 3H data. The GNIP station of San Pellegrino in Alpe is the closest station available (its location was discussed at point 7) and is characterized by annual weighted averages of 6.8 and 8.3 T.U. respectively. Other stations, such as Genoa and Pisa, showed values slightly lower, ranging from 5.5-5.8 T.U. to 6.7-7.3 T.U. respectively.

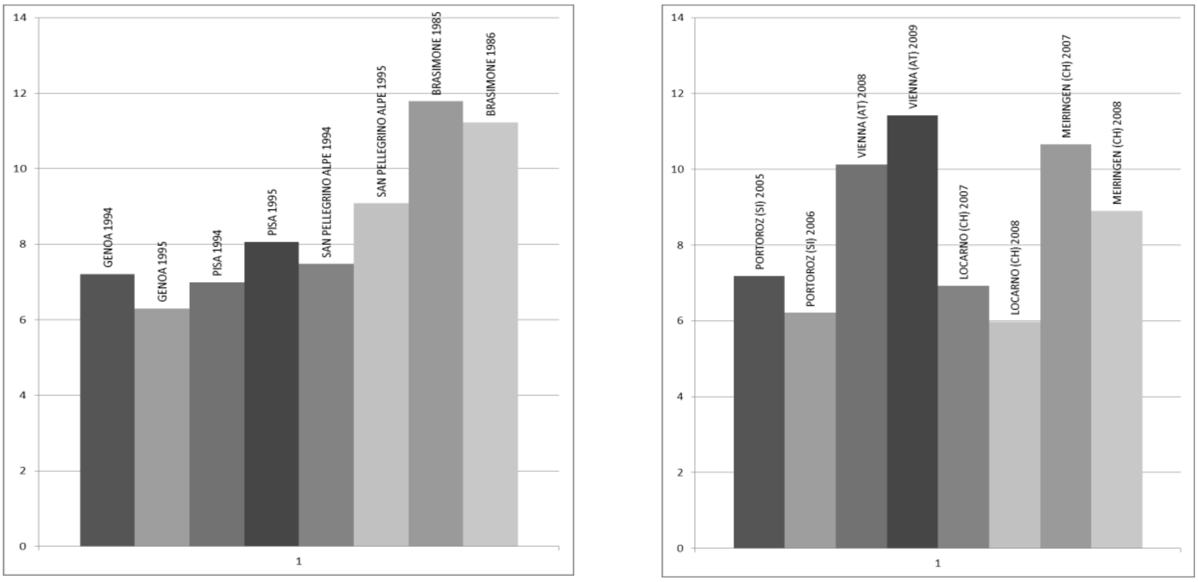
With specific reference to Genoa station, it must be mentioned that Dadomo and Martinelli (2005) provided a detailed comparison of 3H data from this stations and they concluded that 3H values in the northern Apennines are generally 20-25% higher than the corresponding values measured in Genoa. The authors explained this relative enrichment as a results of a different atmospheric/precipitation regime, i.e. they confirmed a continental effect as previously noticed by Ferronsky and Polyakov (2012).

Other GNIP-IAEA stations located in foreign countries have also been taken into account after the suggestion of the reviewer. Slovenia (Portoroz), Austria (Vienna) and Switzerland (Locarno, Meiringen) stations were active up to 2009 and, starting from the 2004, showed annual weighted values ranging from 5.3 (Locarno, 2003) to 14.7 T.U. (Meiringen, 2005).

Among them, some differences could be noticed. In particular, a geographical control in 3H seems to be present: two “clusters” can be identified and allow us to define “coastal-near lake” stations (such as Portoroz and Locarno: mean value of 7.3 and 6.6 T.U. respectively) and “continental” stations (Meiringen and Vienna: values around 11.7-10.9 T.U. respectively). In addition to that, no 3H decreasing trends could be detected for this time-windows and no values lower than 5 in recent rainfalls (up to 2009) were measured, even in coastal areas.

In conclusion, the considerable variability observed for the same periods in areas close to northern Apennines highlights problems of reliability in the selection of the tritium values belonging to the rainfalls for Ca' Lita site.

So we still believe that the presence of a complete tritium record of three-monthly dataset from the ARPA report, which referred to the same hydrologic year that we have analysed in Ca' Lita and to the same river basin of Ca' Lita, provides more representative values of T.U. than those available from the GNIP-IAEA stations. Such a tritium record (obtained using the same analytical method used in Ca' Lita, which is described in the paper) shows that T.U. is in average of 9.8 T.U., with small variability throughout the year. These data are comparable to those collected by Tazioli (2011) in a rain-gauge located in the eastern-sector of the Apennines, close to the Adriatic sea (Monte San Vicino, Marche region): for the 2008-2009, the weighted average was 8.4 T.U.



Italy (stations closer to the test site)

Europe (stations from selected locations)

Plots of 3H (T.U.) from GNIP-IAEA database.

On these basis, the following considerations can be made:

- The assessment of a mean 3H value for rainfall is required in our research for calculating slope water balance.
- There is a kind of objective difficulty (see above) in establishing a precise value of 3H. As correctly asserted by the Referee, the best way could be represented by a rain-gauge located at the Ca' Lita site, with a direct assessment of the tritium contents. Unfortunately, due to the high costs required for implementing such monitoring system, it has been decided to use a three-monthly dataset provided by ARPA for the same hydrologic year and from a superficial well close to the site. At any rate, it represents a mean value of 3H for rainfall more correct than others that could be taken from stations belonging to GNIP-IAEA database. Furthermore the few stations GNIP-IAEA closer to Ca' Lita cannot be used as they stopped collecting data in 1995.
- A value of 3H equal to 5 T.U., that has been proposed by the referee for recent precipitation, has been detected along some coastal areas of the Mediterranean during the winter periods, but it is an underestimated annual average of 3H values for the northern Apennines, where a stronger continental influence exists. So we still believe that the value of 9.8 T.U. for 2009 reported by ARPA as more realistic and representative of local conditions in Ca' Lita than data form GNIP-IAEA network.

Intended consequent amendments to the paper:

- ✓ Improve reference to ARPA dataset and introduce and discuss conclusions from Dadomo and Martinelli (2005) and Tazioli (2011).
- ✓ Introduce a brief discussion on the GNIP-IAEA dataset.

Cited references:

- Dadomo A., and Martinelli, G.: Aspetti di Idrologia Isotopica in Emilia-Romagna. In: Giornata Mondiale dell'Acqua. Acqua e copertura vegetale. In: Atti dei Convegni Lincei, Accademia Nazionale dei Lincei, 216, 161-170, 2005.
- Ferronsky, V.J., Polyakpov V.A.: Isotopes of the Earth's Hydrosphere, Springer-Verlag, New York, 682pp, 2012.
- Tazioli, A.: Landfill investigation using tritium and isotopes as pollution tracers, Acquae Mundi, 89-92, 2011.

10) Samples on the evaporation line exhibit also high ion concentrations illustrating that "anomalous" isotopic composition is related to the chemical status of groundwater. These are probably interrelated. Authors should put more efforts to interpret the sources of Cl-, SO42- and B-ions. Their statement that former two are not justified with the local mineralogy is not acceptable. Based on my knowledge it seems that these ions are coming from evaporate minerals and if these hypothesis is valid the end member for mixing can be connate water from evaporate deposits. It is very unlikely that such concentrations will come from oxidation processes of sulphide minerals. Also some efforts should be put in their interpretation of the relation between Cl- and SO42- ions that will help to clear out their origin. At the same time authors should check hypothesis if some on-site concentrating processes are possible. This can happen as a consequence of evaporation that is unlikely here or with suction processes through the low permeable soil (sediment).

Short reply:

We do not agree with the reviewer but will extend our discussion to better explain our arguments and also discuss the points raised by the reviewer.

Long reply:

Our statement that the local mineralogical composition cannot explain the high conductivity and the presence of some ions (as, for example, Cl-) in Ca' Lita groundwater (DrA) is based on a set of quali-quantitative analyses carried out on the soil samples by diffractometry. Results, which were presented in the paper, showed that no Cl minerals are present. How could the Cl- be concentrated in groundwater if no mineralogical phase can provide? That has been confirmed by the 10h leaching-tests: Cl- has not been released into the deionized water. An equilibrium approach soils-rainfall has been tested by applying Phreeqc modeling. Even at the equilibrium Cl- is not observed.

Moreover, in the northern Apennines, the only units that could contain Cl- belongs to the Triassic evaporites (TUG, as described in the Geological settings chapter in our manuscript). This last contains halite (NaCl) but, as clearly shown in the cross section of Fig. 1B, is locally at a depth of about 10 km. In addition, these evaporites cannot release such high B- ions values, as perhaps observed in some karst springs discharging from the same geological formation (Poiano springs in Toscani et al, 2001). As reported by several authors (please see references at point 12), it is unlikely that an exchange process can release B- into water from active clay. In fact, it should require higher temperatures than those characterizing the study site.

In conclusion, it is very unlikely that these ions might concentrate due to an evaporation process, as it they are not significantly present in origin. Furthermore, if we exclude thenardite (Na2SO4), which is a secondary phase that could be detected in Ca' Lita, there are no mineralogical phases from evaporite units.

It is much more likely that their origin is related to saline waters associated to hydrocarbon deposits. They are strongly enriched in Cl- and B- and they are widely reported in the middle-front part of the chain (as represented in Fig 1.a; Videpi project, Buttinelli et al., 2011) focusing their discharge along tectonic lines. Furthermore, data from Ca' Lita have also been compared with several samples collected in the northern Apennines, by providing appropriate number of literature references (a fact that is acknowledged by the reviewer). .

As reported in literature (Mazor, 1997), B- and Cl- are among the most diagnostic and stable elements that could be utilized. B- can actually be absorbed by clay minerals constituting the landslide deposit, but it can hardly be released by exchange processes in amounts so high to justify the values noticed in Ca' Lita (please see the point 12) . We would also like to pinpoint that the northern Apennines are constituted by clay-rich formations, but high B- values in water are very infrequent.

Finally, we agree with the referee when he states that the mixing could be the relevant process, but the second end-member cannot be identified as connate water. In the northern Apennines, connate water have been reported for the only QM unit, along the boundary with the Po plain (i.e. mud volcanoes). This unit, that is made up by pliocenic marine clay, has not been involved by strong burial processes and so it has not been over-consolidated. As a results, these clays can be impregnated by marine water related to the old pliocenic sea. Anyway, this is not the case of Ca' Lita: the QM unit doesn't outcrop and is not even present at depth (as clearly shown even by the geological section Fig.1b). Moreover, during the several orogenic phases that built up the Apennine wedge, the Ligurian unit LU outcropping in the Ca' Lita site has been interested by high tectonic stresses that resulted in overconsolidation, a process that implies that no connate water can remain entrapped.

Intended consequent amendments to the paper:

- ✓ Include some of the above mentioned further considerations in the discussion

Cited references:

- Mazor, E.: Chemical and Isotopic Groundwater Hydrology, Marcel Dekker Inc., New York, 413 pp., 1997.
- Toscani, L., Venturelli, G. and Boschetti, T.: Sulphide-bearing Waters in Northern Apennines, Italy: General Features and Water-rock Interaction, Aquat. Geochem., 7 (3), 195-216, 2001.

11) Among analyses at the disposal Cl- concentrations can be understood as more conservative than d18O. Why is chloride not using for end member mixing model? With alternative use of d18O and Cl- consistency of interpretation can be checked.

Short reply:

We do not agree

Long reply:

Boschetti et al. (2010) showed that the amount of Cl- in wells belonging to the VIDEPI network is highly variable. The same authors presented values of δ18O that are much less variable and, therefore, much more constrained. As the Cl- content in the end-member represented by oil field water is unknown, we therefore opted for using δ18O only.

Intended consequent amendments to the paper:

- ✓ Include the above mentioned considerations in the discussion
- ✓ Include citation of the work of Boschetti et al., 2010 .

Cited references:

- Boschetti, T., Toscani L., Shouakar-Stash O., Iacumin P., Venturelli G., Mucchino C., and Frape, S.K.: Salt Waters of the Northern Apennine Foredeep Basin (Italy): Origin and Evolution, Aquat. Geochem., 17(1), 71-108, 2010.

12) Some caution is needed in the interpretation of Btot concentrations. B species are not conservative as Cl- ion is. Their concentrations can be very much influenced by the mineralogy of the clay in the aquifer and consequently absorbed or desorbed.

Short reply:

We do not agree

Long reply:

As already discussed in the reply to comment 10, we believe that B- and Cl- are rather diagnostic and stable elements. In particular, the use of B- allowed further comparison with a huge amounts of data that have been published in literature.

The reviewer's statement that "concentrations can be very much influenced by the mineralogy of the clay in the aquifer and consequently absorbed or desorbed" is on our opinion only partially correct, particularly when active (for B-) clays such as illites are involved.

As evidenced by several authors (Grew and Anovitz, 1996; Walker, 1975), B- can hardly be adsorbed or released by clay minerals at the site temperature. Keren and Mezuman (1981) discussed several batch experiments and confirmed that, even considering samples completely composed by illite or montmorillonite, B- can be adsorbed in very small quantities only if peculiar pH conditions take place (pH in the range of 9-

10). This is not our case, as the pH detected in DrA was neutral (pH=7.3-7.6) and the illite component (the most active for the B-) has been assessed to be only about 13,8% in the MOH sample.
On the other hand, Couch (1971) and Eriksson et al. (1996) highlighted adsorption processes in marine environments. But they also highlighted that once B- is adsorbed into clay minerals, it becomes fixated by hydrogen bonding (Couch, 1971). In this way, it is incorporated into the tetrahedral sheet structures and it cannot be released unless temperature increases significantly.
Therefore, while a possible adsorption process in Ca' Lita could eventually be admitted, a B- release from clays at normal temperatures is believed to be very unlikely.
Moreover, another possible limited source of B-, such as halite dissolution, has to be excluded in Ca Lita, as such mineral phase is not present in the slope and not even at depths (see point 4).
For this reason, the high amount of B- in Ca' Lita groundwater can only be explained by assuming an external source of B- feeding the aquifer.

Intended consequent amendments to the paper:

✓ Include references cited in reply

Cited references:

- Grew, E. S. and Anovitz, L. M.: Boron: mineralogy, petrology and geochemistry, Rev. Mineral., 33, 864 pp., 1996.
- Walker, C. T.: Geochemistry of Boron, Dowden, Hutchinson & Ross, Benchmark Papers in Geology, Stroudsburg, PA, 23, 414 pp., 1975.
- Keren, R., and Mezuman, U.: Boron adsorption by clay minerals using phenomenological equation, Clays and Clay Minerals, 29 (3), 198-204, 1981.
- Couch, E.L., 1971. Calculation of palaeosalinities from boron and clay mineral data. Bull. Am. Assoc. Pet. Geol., 55: 1829-1837.

13) At the end of the paper based on the mixing model conclusion is reached that deep water component is in the range of 7,800 to 17,500 m3/year. In fact this is small quantity between 2.5x10-4 to 5.5x10-4 m/s. Authors should somehow comment reliability of their water balance. The numbers of the deep water flow are much smaller than the error of the estimated evapotranspiration and surface water component that are very roughly estimated and not measured. For the latter they are even playing with estimated surface run-off coefficient.

Short reply:

We partially agree, but it was not the aim of the paper to estimate the most exact water balance, but rather to integrate the discussion on the deep origin of an aliquot of groundwater by providing a semi-quantitative assessment and to compare it with the total groundwater balance.

Long reply:

As already explained in point 9, the water balance is unavoidably affected by some uncertainties that are related to the methodology used. In our study, we decided to use a common and worldwide accepted soil-water balance assessment that is based on the Thorntwaite and Mater (1957) formula. The method has been applied at the annual hydrologic – scale. We provided a range of runoff coefficient values as reported by Civita (2005) for the common flysch outcropping in the northern Apennines. As correctly indicated by the reviewer, this reference is actually missing and we intend to include it.

By starting from the consideration that the uprise of deep water is present, we tried to consider it as part of the water balance. And if results show that the aliquot of deep water flow is smaller than the error of the estimated evapotranspiration, this does not mean that deep water inflow is not present or should be neglected.

Nevertheless, as the reviewer is partially right (uncertainties in runoff coefficient are inevitable, since we have no direct measure of it) we have decided to provide different scenarios of runoff coefficient in order to providing a range of plausible results (a sort of sensitivity analysis).

Intended consequent amendments to the paper:

- ✓ Introduce reference to the work of Civita for runoff coefficients

Cited references:

- Civita M.: Idrogeologia applicata e ambientale, Casa Editrice Ambrosiana, Milano, 794 pp., 2005.

REPLIES TO SPECIFIC COMMENTS TO THE PAPER

1) Throughout the paper all ions must be written in ionic form (e.g. Cl- and not Cl) and where concentrations measured as total reported as such (e.g. Btot). Writing without indexes for ions is not in accordance of IUPAC standards. The same is valid for the diagrams.

2) Through the paper in reporting isotope compositions unit for permile ‰ must be strictly used. According to the accepted professional standard in isotope geochemistry literature is not permitted to write results of isotopic composition without unit. The same is valid for the diagrams.

3) Precision and accuracy of isotopic measurements should be reported. Based on these data numbers in Table 3 must be properly rounded and interpreted in the text.

Short cumulative reply:

We agree

Long cumulative reply:

For the last point, we completely agree with the referee. As described in the Methods section, Oxygen-18 and deuterium were assessed by Thermo Delta Mass Spectrometer in ARPA laboratories, Piacenza, Italy. The precisions are in the order of ±0.1‰ and ±1‰ respectively.

Tritium analysis was performed using the electrolytic enrichment and liquid scintillation counting method (Thatcher et al., 1977) at the Hydroisotop laboratory of Munich, Germany (±0.1 to 0.2 TU at 1 Sigma).

Intended consequent amendments to the paper:

✓ We will implement the paper according to specific comments 1, 2, 3.