“Groundwater mean transit times, mixing and recharge in faulted–hydraulic drop alluvium aquifers using chlorofluorocarbons (CFCs) and tritium isotope (^{3}H)” by Ma, B., Jin, M., Liang, X., Li, J., Hydrol. Earth Syst. Sci., doi:10.5194/hess-2018-143.

We appreciate the many valuable suggestions and helpful comments of **Anonymous Referee #1**. We have seriously considered all of the suggestions and comments and have attempted to address each of the comments point-by-point. Detail explanations are as follows.

Author’s response – Line numbers referring to the old and revised version manuscripts are preceded by L and RL, respectively.

Anonymous Referee #1

General Comments

The paper reports CFC, tritium, carbon-14 and stable isotope measurements for groundwater in the Manas River Basin in China and uses them to estimate mean transit times for the complex mixtures of groundwaters in the area resulting from the complicated geology.

The complications of the subject combined with English that is not quite right make this a difficult read. However, the paper addresses relevant scientific questions suitable for publication in HESS, with novel concepts and ideas. Substantial conclusions are reached.

The methods are valid and described satisfactorily, and title and references are well done. There is a problem with the abstract (see below) and consequently the overall structure needs improvement. Some of the figures are complex and could be explained better.

Response: We would like to thank you very much for taking the time to review our manuscript and for their generally positive feedback. We will ask a proof reader to modify the language to help improve readability. We have reorganized the structure and tried our best to present a clear roadmap to readers. We also agree with you that some of the figures are complex which have also been pointed out by Ref #2.

The outline of the manuscript have been reorganized as follows:

Title: Application of environmental tracers for investigation of groundwater mean residence time and aquifer recharge in faulted–hydraulic drop alluvium aquifer

1. Introduction
2. Geological and hydrogeological setting
3. Materials and methods
    3.1 Water sampling
    3.2 Analytical techniques
    3.3 Groundwater dating
        3.3.1 CFCs indicating modern water recharge
        3.3.2 The apparent ^{14}C ages
        3.3.3 Groundwater mean residence time estimation
4. Results and discussion

- 4.1 Stable isotope and major ion hydrochemistry
- 4.2 Modern and paleo–meteoric recharge features
    - 4.2.1 Stable isotope indications
    - 4.2.2 CFCs indications
    - 4.2.3 ^{3}H and ^{14}C indications
- 4.3 Groundwater mean residence time
    - 4.3.1 ^{3}H and CFCs
    - 4.3.2 Hydrochemistry evolution

5. Conclusions

Figures 6, 8 and 9 have been redrawn as follows:

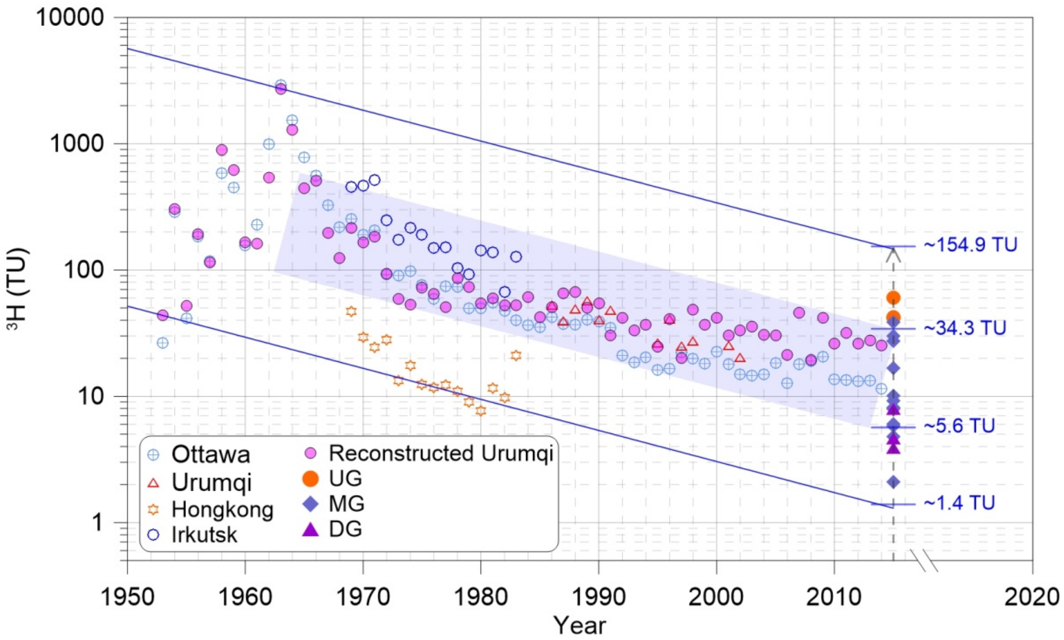

Figure 6. Tritium concentration (TU) of groundwater water samples of upstream groundwater (UG), midstream groundwater (MG), and downstream groundwater (DG). Time series of tritium concentration in precipitation at Ottawa, Urumqi, Hongkong, and Irkutsk were obtained by GNIP in IAEA (https://www.iaea.org/). The blue dashed lines and shaded field were drawn using the half–life (12.32 yrs) of tritium decayed to 2014. (It is Fig. 4 in the revised manuscript)

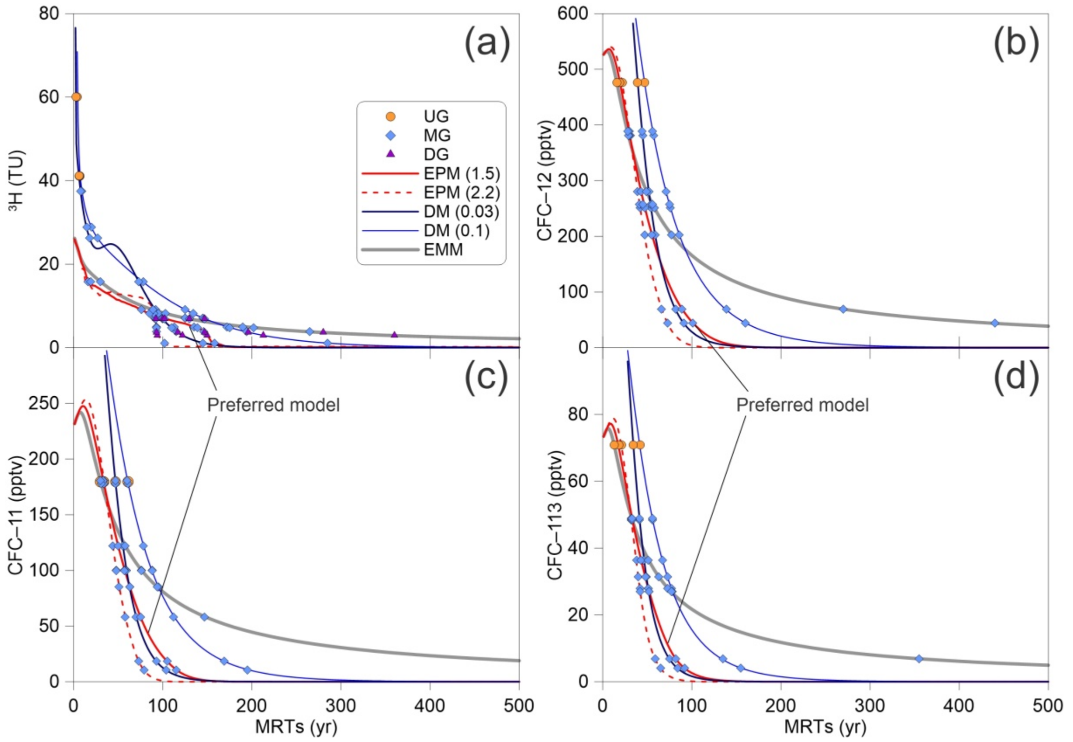

Figure 8. Tritium and CFCs (CFC–11, CFC–12 and CFC–113) output vs. mean residence times for different lumped–parameter models estimated using Eqs. (2) to (5). The input ^{3}H activity and CFCs concentration are using the estimated ^{3}H activities in precipitation in Urumqi station (Fig. 4) and Northern Hemisphere atmospheric mixing ratio (Fig. 3), respectively. (It is Fig. 10 in the revised manuscript)

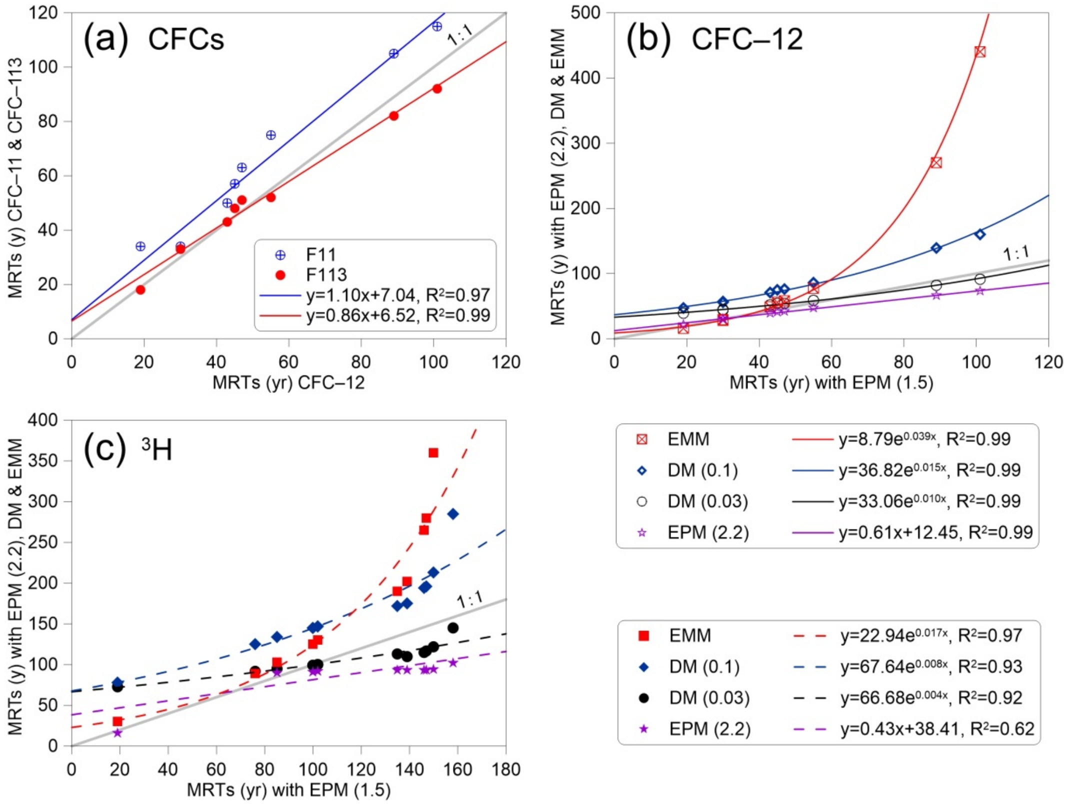

Figure 9. (**a**) MRTs with EPM (1.5) of CFC–12 vs. CFC–11 & CFC–113, (**b**) CFC–12 MRTs with EPM

(1.5) vs. EPM (2.2), DM & EMM, and (**c**) 3H MRTs with EPM (1.5) vs. EPM (2.2), DM & EMM. (It is Fig. 11 in the revised manuscript)

Specific Comments

1) A major problem is that there appears to be a disconnect between the abstract/conclusions and the rest of the paper. The following sentence from the abstract/conclusions:

“The thrust faults were found to play a paramount role on groundwater flow paths and MTTs due to their block water features, where the relatively long MTTs were found near the Manas City with shorter distance and smaller hydraulic gradients.”

is not supported by any discussion in the paper. Yes, it may be supported by implication from the results, but such support needs to be made explicit (possibly in its own subsection since this is an important conclusion).

Response: This sentence has been deleted. To make the abstract and conclusions to be more clear and well-founded, we have revised the abstract/conclusions and delete some incorrect statements. Yes, this conclusion is important but not supported by strong supporting evidences in the paper. Indeed, there are some results that show large differences on both sides of the thrust fault. For examples, there is a level difference of 130 m hydraulic drop (Fig. 1c) in the south margin in Shihezi (SHZ), ^{3}H activities of groundwater decrease rapidly along the Manas River motion in the north of the fault but show relatively the highest values in the south of the fault (Fig. 8). These results still can not support the conclusion explicitly “The thrust fault were found to play a paramount role on groundwater flow paths …”.

The revised abstract is as follows (RL12–26):

“Documenting the groundwater residence time and recharge source is crucial for water resource management in the alluvium aquifer of arid basin. Environmental tracers (CFCs, ^{3}H, ^{14}C, δ^{2}H, δ^{18}O) and hydrochemistry of groundwater were used to assist our understanding of groundwater mean residence times (MRTs) and aquifer recharge in faulted–hydraulic drop alluvium aquifers in the Manas River Basin (China). The very high ^{3}H activities (41.1–60 TU) of groundwater in the Manas River upstream (south of the fault) indicate the rainfall recharge during the nuclear bomb (since the 1960s). Carbon–14 groundwater ages increase with distance (3000–5000 yrs in the midstream to > 7000 yrs in the downstream) and depth, as well as with low ^{3}H activities (1.1 TU) and more depleted δ^{18}O values, confirming that the deeper groundwater is derived from paleometeoric recharge in the semi–confined groundwater system. MRTs estimated using an exponential–piston flow model vary from 19 to 101 yrs for CFCs and from 19 to 158 yrs for ^{3}H, which show much longer MRTs for ^{3}H than CFCs may be due to the time lag through the thick unsaturated zone. The remarkable correlations between CFCs rather than ^{3}H MRTs and pH, SiO_2 and SO_4^{2-} concentrations allow first–order proxies of MRTs for groundwater at different times to be made. Quite ‘modern’ recharge is found in the south of the fault with young (post–1940) water fractions of 87–100 %, while in the north of the fault in the midstream area the young water fractions vary from 12 to 91 % based on the CFC binary mixing method. This study shows that the combination of CFCs and ^{3}H residence time tracers have potential to study groundwater MRTs and identify the recharge sources for the different mixing end–members.”

2) The meaning of the phrase “block water features” is not clear, possibly it means areas where there are strong (semi-vertical) contrasts in hydraulic conductivity (due to the thrust faults).

Response: Yes, the phrase “block water features” is not a very appropriate statement in this paper. What we want to tell the reader is that there are strong contrasts in hydraulic conductivity due to the thrust fault. The variant hydraulic conductivity also can be reflected by the geological and hydrogeological settings. Previous studies (Wu, 2007; Zhao, 2010) and other geological survey works in the Manas River Basin have indicated that the thrust faults shown in Fig. 1b are compressional faults and thus of water–blocking feature, which can explain the “a level difference of 130 m hydraulic drop is observed due to the thrust fault in the alluvium aquifer (Fig. 1c)”.

A recent study by Bresciani et al (2018) has distinguished the mountain–front recharge (MFR) and mountain–block recharge (MBR) by using hydraulic head, chloride and electrical conductivity data in the arid basin. MFR predominantly consists of stream infiltration in the mountain–front zone, and MBR consists of subsurface flow from the mountain towards the basin. Manas River Basin aquifers may receive the recharge from the south mountain through the MFR mechanism, and more specific analysis will be carried out in the future work.

3) Use of “apparent” ages in the preliminary discussion (Section 4.2.1) is defensible as described.

Response: We find that the phrase “apparent CFC ages” has been widely used in many other literatures (e.g. Darling et al., 2012; Hagedorn et al., 2011; Han et al., 2012; Happell et al., 2006; Koh et al., 2012; Plummer et al., 2006; Qin et al., 2011, 2012). However, a review paper by Suckow (2014) pointed out that the “apparent age” is “only well defined if the formula is given and if the tracer is stated”. There are appropriate formulas for different tracers, such as ^{14}C, ^{36}Cl, ^{81}Kr, ^{3}H/^{3}He, and so on, but not for the CFCs, for SF_6 and for ^{85}Kr. Therefore, Suckow (2014) thinks that, strictly speaking, the term “apparent age”, should not be used for CFCs. This erroneous term “apparent age” for CFCs is also pointed out by Ref #2 (“L277: The paragraph on “apparent age” makes no sense for … and sampling”).

We agree that the term “apparent age” for CFCs will not be used anywhere in our paper. As we know that the CFCs are synthetic organic compounds and largely released to the air since 1930s, and thus they have been regarded as very good tracers for dating young water recharge time (post–1940 recharge). Therefore, we would like to use CFCs to explain the modern water recharge features.

The revised contents can be seen in Section 3.3.1 (RL172–192) and in Section 4.2.2 (RL344–414):

Section 3.3.1 (RL172–192):

“Knowledge of the history of the local atmospheric mixing ratios of CFCs in precipitation is first required for indicating modern water recharge. The difference between the local and global background atmospheric mixing ratios of CFCs (Northern Hemisphere), which we intitule as CFC excess, varies largely based on the industrial development. Elevated CFC concentrations of 10–15 % higher than those of the Northern Hemisphere have been reported in the air of urban environments such as Las Vegas, Tucson, Vienna and Beijing (Barletta et al., 2006; Carlson et al., 2011; Han et al., 2007; Qin et al., 2007), while in Lanzhou and Yinchuan (northwest China) were about 10 % less (Barletta et al., 2006). In this study, Manas River Basin locates in the northwest of China (Fig. 1a) with very low population density and is far from the industrial city. To evaluate CFC ages, the time series trend of Northern Hemisphere atmospheric mixing ratio (1940–2014, http://water.usgs.gov/lab/software/air/cure/) was adopted in this study.

Measured CFC concentrations (in pmol L^{-1}) can be interpreted in terms of partial pressures of CFCs (in pptv) in solubility equilibrium with the water sample based on Henry's Law solubility. Concrete computational process was followed that by Plummer et al. (2006a). In the arid northwest China, the local shallow groundwater temperature was more suitable than the annual mean surface air temperature to be estimated for the recharge temperature (Qin et al., 2011) as the local low precipitation usually cannot reach the groundwater. Previous studies in MRB (Ji, 2016; Wu, 2007) have also indicated that much less vertical recharge water from the local precipitation as compared to the abundant groundwater lateral flow recharge and river leakage from the mountain to the piedmont areas. In this study the measured groundwater temperature that vary from 11.5 to 15.7 ºC from each well (Table 1) as the recharge temperature was used to estimate the groundwater input CFC concentrations. Surface elevations of the recharge area vary from 316 to 755 m. The modern water recharge is then determined by comparing the calculated partial pressures of CFCs in solubility equilibrium with the water samples with historical CFC concentrations in the air"

Section 4.2.2 (RL344–414):

"It is seen from Table 1 that groundwater with well depths between 13 and 150 m contain detectable CFC concentrations (0.17–3.77 pmol L^{-1} for CFC–11, 0.19–2.18 pmol L^{-1} for CFC–12, and 0.02–0.38 pmol L^{-1} for CFC–113) both in the upstream and midstream areas, indicating at least a small fraction of young groundwater components (post–1940). The highest concentration was observed in the UG (G3), south of the fault, median and the lowest were respectively observed in the west and east bank of the 'East main canal' in the MG, north of the fault. In the midstream area (Fig. 2), CFC concentrations generally decrease with well depth at the south of reservoirs (G25, G8, and G9), while increase with well depth at the north of reservoirs (G15 and G16), which might indicate the different groundwater flow paths (e.g., downward or upward flow directions).

Groundwater aerobic environment (Table 1, DO values vary from 0.7 to 9.8 mg L^{-1}) make CFC degradation under anoxic conditions unlikely. Nevertheless, CFC–11 has shown a greater propensity for degradation and/or contamination than CFC–12 (Plummer et al., 2006b). Therefore, we use the CFC–12 to interpret the modern groundwater recharge in the following discussions. The estimated CFC atmospheric partial pressures and possible recharge year are shown in Table 2 and Fig. 3. The UG (G3) CFC–113 and CFC–12 both indicate the 1990 precipitation recharge (Table 2), probably indicating piston flow recharge in the upstream area. The MG CFC–11–based modern precipitation recharge agreed within 2–8 yrs with that based on CFC–12 concentrations, while that the CFC–113–based recharge were much 4–11 yrs later than that based on CFC–11 and CFC–12 concentrations, indicating mixtures of young and old groundwater components recharge in the midstream area. The latest groundwater recharge is in the upstream area (G3 with 1990 recharge), which is most likely due to the shortest flow paths from recharge sources compared to the piedmont groundwater samples in the midstream area.

Groundwater G5 and G7, which are located in the East 'East main canal' in the midstream area with much shorter distance than G15 and G16 in the reservoir north, show that the modern recharge are much earlier than G15 and G16 (Table 2). This could be explained by the lower groundwater velocities in the East 'East main canal', where the hydraulic gradient (Fig. 2) is much smaller than the West. Furthermore, it can be seen from Table 2 and Fig. 2 that groundwater recharge were much earlier with well depth increasing from 48 to 100 m at the reservoir south (G25, G8 and G9), while that in the reservoir north were much later with well depth increasing from 23 to 56 m (G15 and G16). The different trends for the relationship between groundwater recharge year and well depth might be ascribed to the different flow paths among the two sites (e.g., reservoir south and north).

Comparing CFC concentrations has provided a powerful tool to recognize samples containing co–existence of young (post–1940) water with old (CFC–free) water (Han et al., 2007; Han et al., 2012; Koh et al., 2012) or exhibiting contamination or degradation (Plummer et al., 2006b). The cross–plot of the concentrations for CFC–113 and CFC–12 (Fig. 7a) demonstrates that all of the groundwater can be characterized as binary mixtures between young and older components, though there is still room for some ambiguity around the crossover in the late 1980s (Darling et al., 2012). As shown in Fig. 7a, all of the MG samples are located in the shaded region, representing no post–1989 waters recharge. The UG (G3) sample is clearly quite 'modern' and seems to be recharged in 1990 through piston flow or mixed by the old water and post–1989 water. Using the method described by Plummer et al. (2006b) with the binary mixing model (BMM), the fractions of young water vary from 12 to 91 % (Table 2) for the MG samples with the relatively low young fractions of 12 and 18 % in the east bank of the 'East main canal' of MG samples (G5 and G7). These two well water table depths are more than 40 m, probably indicating a relatively slow and deep circulated groundwater flow. This hypothesis is also suggested by lower DO (3.7–4.6 mg L^{-1}; Table 1) and nitrate concentrations (8.6–9.5 mg L^{-1} from Ma et al., 2018) and relatively much smaller hydraulic gradient (Fig. 2). Furthermore, as high as 100 % fraction of young water for G3 sample is obtained with the recharge water from 1990, or 87 % fraction is obtained by the binary mixture between post–1989 water and old water (Table 2). The quite 'modern' recharge for G3 sample is likewise explained by its highest DO (9.8 mg L^{-1}; Table 1) and relatively low nitrate concentration (7.9 mg L^{-1} from Ma et al., 2018), which represent the contribution of high–altitude recharge rather than the old age water.

CFC contamination and sorption in unsaturated zone during recharge have great influence on interpretation of groundwater recharge. Points lying off the curves in the cross–plot CFC concentrations may indicate that contaminations from the urban air with CFC compounds during sampling (Carlson et al., 2011; Cook et al., 2006; Mahlknecht et al., 2017) or degradation/sorption of CFC–11 or CFC–113 (Plummer et al., 2006b). Figure 7 demonstrates that the urban air with CFC compounds contaminations, which generally cause elevated CFC concentrations than the global background atmospheric CFC concentrations (Northern Hemisphere), are unlikely. Elevated CFC concentrations have been reported in the air of urban environments such as Las Vegas, Tucson, Vienna and Beijing (Barletta et al., 2006; Carlson et al., 2011; Han et al., 2007; Qin et al., 2007), contrary to that in the arid northwest China (Barletta et al., 2006). Hence, the anomalous CFC–11/CFC–12 (Fig. 7b) ratios plotting off the model lines might be ascribed to the sorption in the unsaturated zone during recharge rather than the degradation of CFC–11 (Cook et al., 2006; Plummer et al., 2006b) under anoxic conditions (Table 1, DO values vary from 0.7 to 9.8 mg L^{-1}). Nevertheless, the small deviations (Fig. 7b) indicate that the hypothesized sorption rate was low. Higher CFC sorption rate with high clay fraction and high organic matter in soils have been proved (Russell and Thompson, 1983), and vice versa (Carlson et al., 2011). Therefore, the hypothesis of a low sorption rate due to the low clay fraction and low organic matter content in the intermountain depression and the piedmont plain (Fig. 1c) seems reasonable.

The time lag for CFCs transport through the thick unsaturated zone (Cook and Solomon, 1995), as well as degradation especially for CFC–11 is being common in the anaerobic groundwater (Horneman et al., 2008; Plummer et al., 2006b), which both are important consideration when interpretation of groundwater recharge using CFC concentrations. The time lag for CFCs movement both in dissolved and gas phases through deep unsaturated zone. The time lag for the diffusive transport of CFCs through deep unsaturated zone in simple porous aquifers, a function of the tracer solubility in water, tracer diffusion coefficients and soil water content (Cook and Solomon, 1995), have been widely proved (Darling et al., 2012; Qin et al., 2011). The small differences in CFC–11 and CFC–12 recharge years (Table 2) demonstrates that the time lag would be short in the faulted–hydraulic drop alluvium aquifers with deep unsaturated zone (Fig. 1c). Previous studies in the Manas River Basin (Ma et al., 2018; Wang, 2007; Zhou, 1992) showed that groundwater were mainly recharged by the river fast leakage in the upstream area and piedmont plain, where the soil texture is consisted of pebbles and sandy gravel (Fig. 1c), which makes us to assume that the unsaturated zone air CFC closely follows that of the atmosphere and thus the recharge time lag through the unsaturated zone is not consideration."

4) Strictly, groundwater has "residence time" or "mean residence time"/"MRT" (being the time water takes to travel through a groundwater system to where it is sampled by a bore), rather than "transit time" or "mean transit time"/"MTT" which is generally reserved for streamflow (being the time for water to transit through the catchment and into the stream). Consequently, the word "residence" should be substituted for the word "transit" wherever "transit" appears. And also "MRT" for "MTT".

Response: Agree and changes made. The term "transit" was changed to "residence" and term "MTT" was changed to "MRT", and we insisted on the "residence" and "MRT" throughout the manuscript.

We re-read the literatures and found that term "transit time" was numerously used to indicate the time for water to transit through the catchment and into the stream (Cartwright et al., 2018; Cartwright and Morgenstern, 2015, 2016; Hrachowitz et al., 2009, 2010; Morgenstern et al., 2010; Stewart and Morgenstern, 2016). Stewart et al. (2010) pointed out that "Residence time is the time spent in the catchment since arriving as rainfall. Transit time is the time taken to pass through the catchment and into the stream." Leray et al. (2016) have adopted a general but robust definition for the residence time "the amount of time a moving element has spent in a hydrologic system", and considered the terms residence time, transit time, travel time, age, and exposure time as equivalent in their discussions. Custodio et al. (2018) used both residence times and transit times for groundwater samples collected from springs and deep wells. In our study, all of the groundwater samples were collected from the wells/artesian wells. Thus, we tend to use the term "residence" instead of "transit" in our manuscript.

5) A selection of comments on the English are given below, to help the clarity of the writing. There are many other very small infelicities in the English.

Response: We thank you very much for modifying the expressions of the manuscript. We will ask a proof reader to modify the language to help improve readability.

Technical Corrections

1) P1 L24-25 Change to "Quite 'modern' recharge is found in the south of the fault with young (post–1940) water fractions of 87–100 %, …" from "The quite 'modern' recharge in the south of the fault with young (post–1940) water fractions of 87–100 % is obtained, …"

Response: Agree and changes made. The sentence was changed to (RL23): "Quite 'modern' recharge is found in the south of the fault with young (post–1940) water fractions of 87–100 %, while …".

2) P2 L51 “Instead of” not “over for”

Response: Changes made. “over” was replaced by “than”.

3) P2 L53 “closed” not “close”

Response: Agree and changes made. “close” was replaced by “closed”.

4) P3 L89 “common” not “true”

Response: Agree and changes made. “true” was replaced by “common”.

5) P3 L90-91 “Pumping from long-screened wells (of which there are over 10,000, Ma et al., 2018) …” not “Pumping from the long–screened over 10 000 boreholes (Ma et al., 2018) …”

Response: Agree and changes made. The sentence was changed to (RL89–90): “Pumping from long-screened wells (of which there are over 10 000 boreholes, Ma et al., 2018) make groundwater mixing mostly likely.”. Number “10 000” (not “10,000”) is divided in groups of three using a thin space, complying with the “manuscript preparation guidelines for authors”.

6) P3 L93 “result from” not “impacted by”

Response: Agree and changes made. “impacted by” was replaced by “result from”.

7) P3 L94 “insufficiently recognised” not “insufficient recognition”

Response: Agree and changes made. “insufficient recognition” was replaced by “insufficiently recognised”.

8) P4 L106 “total” not “totally”

Response: Agree and changes made. “totally” was replaced by “total”.

9) P4 L107 “intermittently active” not “intermittent activity”

Response: Agree and changes made. “intermittent activity” was replaced by “intermittently active”.

10) P4 L117 “depth” not “buried depth”

Response: Agree and changes made. Word “buried” was deleted.

11) P6 L177 “Manas River Basin” not “MRB”

Response: Agree and changes made. “MRB” was replaced by “Manas River Basin”.

12) P9 L259 & 264 “slope” not “slop”

Response: Agree and changes made. Erroneous “slop” was changed to “slope”.

13) P10 L300 “we use” not “one assign”

Response: Agree and changes made. “one assign” was replaced by “we use”.

14) P10 L304 “increasing” not “elevated”

Response: Agree and changes made. “elevated” was replaced by “increasing”.

15) P11 L323 “indicates a larger fraction of 1960s precipitation recharge for G4 …” not “indicate that more fractions of the 1960s precipitation recharge was occurred for G4 …”

Response: Agree and changes made. The sentence was changed to (RL425–427): “First, ^{3}H activities of groundwater in the upstream area increase from 41.1 (G1 and G2) to 60 TU (G4) with distance indicates a larger fraction of 1960s precipitation recharge for G4 than G1 and G2 groundwater samples”.

16) P12 L370 “generally” not “totally” and “overlap” not “overlapping”

Response: Agree and changes made. “totally” was replaced by “generally”, and “overlapping” was replaced by “overlap”.

17) P13 L397 delete “far”

Response: Agree and changes made. “far” was deleted.

18) P14 L413 “series” not “serious”

Response: Agree and changes made. “serious” was replaced by “series”.

19) P14 L423 “Overall” not “Totally”

Response: Agree and changes made. “Totally” was replaced by “Overall”.

20) P15 L448 “permit” not “permitting”

Response: Agree and changes made. “permitting” was replaced by “permit”.

21) P15 L465 “other sources” not “either source” (?)

Response: Changes made. “, and giving more accurate prediction of the contaminants like nitrate than either source of information” was deleted.

22) P15 L466 “decreases” not “decrease”

Response: Agree and changes made. Erroneous “decrease” was changed to “decreases”.

23) P16 L488 “which did not contribute groundwater recharge” not “which had non–contributes to groundwater recharge”

Response: Agree and changes made. The sentence was changed to (RL552–553): “…, which did not contribute groundwater recharge in the arid northwest China”.

24) P17 L520 delete “have occurred”

Response: Agree and changes made. “have occurred” was deleted.

25) P19 L578 “… area) imply invasion of modern contaminants, …” not “… area), implying the modern contaminants invading, …”

Response: Agree and changes made. The sentence was changed to (RL561): “… area) imply invasion of modern contaminants, which …”.