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Using Environmental Isotopes for Water Resources Evaluation in Altun Kopri Basin, NE Kirkuk

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Abstract:

Recently, the environmental isotopes are adopted to figure out the hydrological processes, recharge areas, flow paths, groundwater origin and the interaction between different watery bodies. Currently, five samples of the rainwater have been collected since January to April 2012, as well as December 2011. Those sampling periods have highest amounts of precipitation events. Meantime, 25 samples of groundwater, 5 of the Lesser Zab River and 3 of overland flow have been picked up during the wet period. The dry sampling of groundwater and the Lesser Zab River has been achieved in summer 2011. The Local Meteoric Water Line lies between Global Meteoric Water Line (GMWL) and East Mediterranean Water Line (EMWL). The lowest, highest and average of δ^{18} O in precipitation are -4.00‰, -3.60‰ and -3.84‰, while δ^2 H equal to -17.20‰, -14.00‰ and -15.60‰ respectively. The ranges of δ^{18} O and δ^{2} H of the Lesser Zab River in dry period are -3.12‰ to -2.82‰ and -12.80‰ to -12.00‰ sequentially. In the wet period, runoff samples are added to the Lesser Zab River. The lowest and highest of δ^{18} O are -5.30% and -4.87% respectively, while δ^2 H extends from -30.00% to -28.65%. Groundwater samples have δ^{18} O and δ^2 H increased with well depths somewhat. Signatures of the wells have been fallen into two groups within two sampling campaigns; dry and wet periods. The first well samples are dropped above the GMWL and the second samples are classified below the GMWL.

Keywords: Stable Isotopes, Local Meteoric Water line, Groundwater Recharge, Isotopic Variation.

استخدام النظائر البيئية في تقييم الموارد المائية في حوض التون كوبري – شمال شرق كركوك

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الخلاصة:

مؤخرا تم اعتماد تطبيقات النظائر لتخمين العمليات الهايدرولوجية ، مناطق التغذية ، مسارات الجريان ، اصل المياه الجوفية اضافة الى الفعاليات المشتركة بين البيئات المائية المختلفة. جمعت خمس عينات مطرية شهريا من منطقة الدراسة خلال كانون الثاني ولغاية نيسان 2012 ، اضافة الى شهر كانون الاول 2011. شهدت فترات النمذجة اعلى كميات مطرية ممكنة. في تلك الاثناء تم التقاط 25 عينة من المياه الجوفية علاوة على 5 عينات مثلت مياه نهر الزاب الاسفل و 3 عينات من مياه السيح المطري. كما تم نمذجة 25 عينة من المولي الحلي عينة مياه جوفية و 5 عينات اخرى من نهر الزاب الاسفل في فترة الصيف 2011. خط المياه المطري المحلي يقع بين خطي المياه المطري العالمي وشرق البحر المتوسط. بلغ اوطئ ، اعلى ومعدل الاوكسجين-18 في العينات المطرية 140% ، 3.60% و 3.84% على التوالي في حين بلغت قيم الديتيريوم في 3.60% من 17.20% ، 14.00% و 15.60% على التوالي. كانت مديات كل من الاوكسجين-18 والديتيريوم في مياه نهر الزاب الاسفل خلال الفترة الجافة من 3.12% الى 2.82% و 12.80% الى 12.00%. اما خلال الفترة الرطبة فقد كانت مديات الاوكسجين-18 30%. الى 1.80% اما الديتيريوم فكانت -30.00% الى 30.65% ممثلة لمياه نهر الزاب الاسفل مع الاخذ بعين الاعتبار مياه السيح المطري. تميزت عينات المياه الجوفية بمحتوى نظائري للاوكسجين-18 والديتيريوم يتزايد مع عمق آبار المياه الجوفية. عموماً هنالك مجموعتان من عينات المياه الجوفية خلال فترتي النمذجة الجافة والرطبة ، احداها وقعت اعلى خط المياه المطري العالمي والاخرى اسفله.

Introduction:

The isotopes have many practical uses in history, medicine and renewable energy. Also, they are applied in development and management of water resources, climate, environment and ecology aspects. It is a modern technique, which is less effort, cost-effective and reliable choice. Moreover, it is considered a paved way to follow hydrological modelling because it conceptualizes the reality. Multi hydrogeological fields still have unobvious and imprecise solutions when applying the conventional methods only. The environmental isotopes are adopted to figure out the processes and areas of recharge, flow paths, groundwater origin and the interaction between different watery bodies.

Stable isotopic compositions of low mass or light elements like oxygen, hydrogen, carbon, nitrogen, and sulfur are normally expressed by delta (denoted as δ) with values in parts per thousand (denoted as ∞) of enrichments or depletions relative to a standard composition [1]. The values of δ are calculated via Formula (1). Several ways are used for comparisons between the δ values of two materials; the higher versus lower values, the heavier versus lighter, the more positive versus more negative and enriched versus depleted.

$$in (\%_0) = (R_{Sample}/R_{Standard} - 1) 1000$$

$$(1)$$
where:

R : Ratio of the heavy to light isotope in the sample or standard

Deuterium (²H or D) and oxygen-18 (¹⁸O) are most stable isotopes in nature that applied in the aquatic environments studies. Most hydrological investigations use isotope labeled water with deuterium (²H₂O or D₂O), oxygen-18 (H₂¹⁸O) or double-labeled water (²H₂¹⁸O) which uncommon relatively [2]. Specifically, ratios of ¹⁶O to ¹⁸O and ¹H to ²H compared to the Standard Mean Ocean Water are adopted currently (Equations 2 and 3).

$$\delta^{2}H(\%_{0}) = \left(\frac{\binom{2}{H} \binom{1}{H}_{sample}}{\binom{2}{H} \binom{1}{H}_{standard}} - 1\right) 1000$$
(2)

$$\delta^{18}O(\%_0) = \left(\frac{\binom{1^8O}{^{16}O}_{sample}}{\binom{1^8O}{^{16}O}_{standard}} - 1\right)1000\tag{3}$$

The study Area:

The selected area is located in north-northeast of Kirkuk City, Northern Iraq. It forms the left side of Altun Kopri basin which lies between latitudes N35° 30' 00"-35° 50' 00" and longitudes E44° 07' 00"-44° 37' 00", with an area of 1175km² figure 1. The Lesser Zab River divides the whole basin into two parts, right bank (northern part) belongs to Erbil province and left bank (southern part) lies in Kirkuk province. Wadi Jolack sub-basin covers 785km²; it has lowest elevation and (semi)-flat zone in the main basin [3]. The Lesser Zab River bounds the study area from north and northwest, whereas the topographic features of intermittent River of Khassa Chai isolate the basin in south and southeast. Towards east and northeast, there are Khalkhalan Dagh Mountains. Conversely, Kani Domlan mountains are surrounded the study area from west and southwest.

Local weather is hot-dry in summer and cold-rainy in winter. Rainfall averages are 65.8mm and 13.6mm in January and May respectively with poorly distribution. Annual total reaches 342.7mm. Potential evapotranspiration is rounded from 38.2mm to 261.1mm in January and July respectively. The annual total average is 1662.9mm. The monthly averages of highest temperature are 43.9 °C in July and the lowest temperature 4.9 °C in January.

The lithostratigraphic sequence outcropping in the study area consists of four lithological units. The oldest three belong to the Late Miocene-Pliocene (fluvial system) subcycle that considers the last one in Tertiary sedimentary cycle (alluvial system). They settled during the Alpine orogeny northern Iraq with clastic rocks transported from raised mountains in (Mio)-Geosyncline area to deposit in a (sub)-continental environments. The recent unit of stratigraphy has age extended to Pleistocene-Holocene known under Quaternary cycle deposits, which are detrital fragments also. Mostly, the oldest deposits are outcropping in the edges of the studied basin, while the youngest covered the mid of basin. The units are identified upwardly from the oldest to recent; Late Miocene-Injana (Upper Fars) Formation, Pliocene-Almukdadya (Lower Bakhtiari) Formation, Pliocene-Pleistocene Bai-Hassan (Upper Bakhtiari) Formation and Pleistocene-Holocene (Quaternary) Deposits [4-5].

Tectonically, Altun Kopri basin locates in the Foothill zone belonged to the Folded Zone. It lies within the Unstable Shelf included in Chemchemal-Butmah subzone, northern Iraq. It is characterized by enormous (anti)-synclines (northwest-southeast) resulted from the Laramide orogeny that started in Cretaceous and reached its peak in Pliocene due to Alpine orogeny [4].



Figure 1-Site view showing the location of selected wells and surface water samples

The left side of Altun Kopri basin features rapid variation of surface and subsurface sediments, in the form of multi aquifers [5]. Bai-Hassan and Almukdadya Formations constitute lithohydrological units of high thicknesses. Quaternary deposits in the basin center have thickness that decreases toward the limbs. The succession of sandstone, gravel and sand interceded with clay is composing

Almukdadya and Bai-Hassan Formations, while gravel, sand, silt and clay form Quaternary deposits (older and younger unconsolidated alluvium and valleys filled deposits) [6].

The main source of recharge is precipitation that percolates into the gravel, conglomerate and sandstone layers. Catchment area is located in east and northeast and the southwest mountainous areas figure 2. Subsurface flow runs from both drainage areas toward the low hills and basin streams to recharge groundwater. There are springs in the northeastward due to outcrops of sandstone, sand, gravel and clayey layers for Bai-Hassan. They are not observed during the field work because of the decline of groundwater levels recently. Runoff moves toward Wadi Jolack through seasonal valleys [7]. Groundwater depth is mostly deep to shallow. Overall, the wells are deeper toward the highest topographical areas; i.e. east or/and northeast as well as western zone. They extend from 20m to 180m. It does not noticed flowing wells in the study area. Table 1 shows the information of undertaken wells. **Field Work:**

The sampling procedure is different from one laboratory to another. Regarding the International Atomic Energy Agency, ground(surface)-water sampling of ¹⁸O and ²H is simple but accompanied with the great care avoiding further fractionation or/and contamination. No filtration or preservation is



Figure 2-Conceptual scheme of the aquifers system in the study area

required, only filling a 50 mL of watering triply rinsed container. The bottles should be double or sealed capped, glass or high density polyethylene. Clear labels of the samples with all details are needed. For precipitation, a separator funnel is used to collect the rainwater drops into the bottle along monthly rainstorms. Finally, make sure the bottles are capped tightly for no taken place a fractionation in-between time of rainfall event and sampling. It is important reducing the likelihood of evaporation, so it is used an isolated thermos box for water samples storage until transportation to analysis laboratory. The isotope effect of evaporation can be significant: a 10% loss of sample results in an isotope enrichment of about 10% in ²H and 2% in ¹⁸O [2]. Five samples of the rain water have been collected since January to April 2012, as well as December 2011. Meantime, 25 samples of groundwater, 5 of the Lesser Zab river and 3 of overland flow have been picked up during the wet period. The dry sampling of groundwater and the Lesser Zab River has been achieved in summer 2011. The analyses of stable isotopes of oxygen and hydrogen have been done by Water Department in the Ministry of Science and Technology of Iraq. It has been used Liquid Water Stable Isotope Analyzer (LWSIA) and Isotopes Ratio Mass Spectrophotometer (IRMS). The analyses results are tabulated via table 1. Tolerant accuracy values of ¹⁸O, ²Ĥ and ³H are 0.2‰, 1.0‰ and 1.0 TU [2]. **Precipitation:**

Notable high ratios of measured ¹⁸O and ²H in the study area are found during spring (March and April) whereas the lowest values are recorded in winter precipitations (December, January and February). The lowest, highest and average of δ^{18} O in precipitation are -4.00‰, -3.60‰ and -3.84‰, while δ^2 H equal to 17.20‰, -14.00‰ and -15.60‰ respectively.

To implement the stable isotopes data of the study area, it should be undertaken the Global Meteoric Water Line (GMWL) as a base line. It defines a relationship between ²H and ¹⁸O ratios in natural terrestrial waters, expressed as a globally average according to VSMOW (Equation 4). The value of linear slope is about 8 and the intercept value is approximately 10 [8]. $\delta^2 H = 8.13 \times \delta^{18} O + 10.8$ (4)

There is high positive correlated relation between δ^{18} O and δ^{2} H, where R² = 0.97 (Equation 5). It is interpreted that the fractionation processes are less than what can be in rainwater samples. The Local Meteoric Water Line (LMWL) can be different somewhat than the GMWL, in terms of slope and intercept, and individual events will have a line different generally from the LMWL. It should be addressed to the most influential factors on isotopic variations of rainwater samples locally. It can say the source of local rainstorms lies between GMWL and East Mediterranean Water Line (EMWL) (Equation 6) figure 3. Knowing the EMWL equivalents Middle East Water Line (MEWL) [9-10]. (5)

$$\delta^2 H = 7.95 \times \delta^{18} O + 14.92$$

 $\delta^2 H = 8.00 \times \delta^{18} O + 22.00$



Figure 3- Plotting the ²H and ¹⁸O of local precipitation versus GMWL, EMWL, IMWL and Erbil-MWL

On the other hand, the stable isotopes values of Erbil station (Erbil-MWL) and Iraq Meteoric Water Line (IMWL) concluded by Al-Paruany (2013) [11] (Equation 7). Both of them have been plotted between GMWL and EMWL figure 3.

 $\delta^2 H = 7.57 \times \delta^{18} O + 11.97$

(7)

(6)

The relation between δ^{18} O and δ^{2} H is termed by the deuterium excess (d-excess) which refers to climatic conditions and moisture sources during evaporation and precipitation. Equation (8) defines the d-excess suggested by Dansgaard (1964). Through table 1, the d-excess of local precipitation ranges from 14.80% to 15.54%, and 15.12% as average. Many factors can affect on d-excess. The conditions of source area are mainly controlled on water vapor and nature of air masses prior condensation to raindrops [10-12]. Apparently, the d-excess values of late period rains are closer to GMWL, owing interlacing of the climatic factors. Spring precipitations have enrichment of isotopic contents than winter rains, and then they are less suffering of depletion fractionation. The climatic overlap of Mediterranean Sea and Arabian Gulf would be lead to seasonal variations of d-excess. $d = \delta^2 H - 8.0 \times \delta^{18} O$ (8)

Table 1	1- Sa	ampling	points	informa	tions and	stable	isotopes	data o	f ground	lwater.	, surface	water	and	rainwater
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Stable Isotopes Ratios of Groundwater (%)											Surface Water Isotopes (‰)						Rainwater (‰)					
Well	Altitude	Depth	Easting	Northing	Dry			Wet		Sample	Dry		Wet		Sample							
	(m)	(m)			$\delta^{18}O$	$\delta^2 H$	D-Excess	$\delta^{18}O$	$\delta^{2}H$	D-Excess		$\delta^{18}O$	$\delta^2 H$	D-Excess	$\delta^{18}O$	$\delta^2 H$	D-Excess		$\delta^{18}O$	$\delta^2 H$	D-Excess	
$W_{1(Lower)}$	408.00	180.00	442815	3936963	-6.60	-34.15	18.65	-6.75	-34.01	19.99	S_1	-3.00	-12.80	11.20	-5.30	-29.60	12.80	R _{1(Dec)}	-4.00	-17.20	14.80	
$W_{2(Lower)}$	405.00	122.00	443219	3941089	-3.28	-20.41	5.83	-3.01	-19.19	4.89	S ₂	-2.82	-12.05	10.51	-4.87	-28.65	10.31	R _{2(Jan)}	-3.95	-16.60	15.00	
$W_{3(Lower)}$	413.00	90.00	441940	3953298	-3.14	-20.12	5.00	-3.05	-20.00	4.40	S_3	-2.90	-12.00	11.20	-4.90	-29.00	10.20	R _{3(Feb)}	-3.88	-15.50	15.54	
W4(Upper)	351.00	100.00	436612	3953088	-5.60	-25.89	18.91	-5.00	-24.90	15.10	S_4	-3.12	-12.78	12.18	-5.12	-29.10	11.86	R _{4(Mar)}	-3.77	-14.70	15.46	
W _{5(Upper)}	374.00	50.00	439317	3940838	-6.00	-46.01	1.99	-6.03	-43.00	5.24	S ₅	-2.87	-12.10	10.86	-5.00	-30.00	10.00	R _{5(Apr)}	-3.60	-14.00	14.80	
W _{6(Upper)}	364.00	50.00	436742	3943197	-6.23	-38.53	11.31	-6.20	-38.30	11.30	Min	-3.12	-12.80	10.51	-5.30	-30.00	10.00	Min	-4.00	-17.20	14.80	
W7(Upper)	337.00	100.00	431236	3946750	-5.93	-31.35	16.09	-5.30	-30.10	12.30	Max	-2.82	-12.00	12.18	-4.87	-28.65	12.80	Max	-3.60	-14.00	15.54	
W _{8(Upper)}	325.00	115.00	424462	3951489	-5.43	-33.09	10.35	-4.88	-30.37	8.67	Mean	-2.94	-12.35	11.19	-5.04	-29.27	11.03	Mean	-3.84	-15.60	15.12	
W _{9(Upper)}	299.00	112.00	425314	3957151	-5.62	-31.99	12.97	-4.93	-33.10	6.34	St. Dev.	0.11	0.36	0.56	0.16	0.47	1.10	St. Dev.	0.14	1.18	0.32	
W _{10(Lower)}	302.00	72.00	446934	3943870	-5.00	-21.31	18.69	-5.12	-21.32	19.64	P ₁				-2.40	-35.00	-15.80					
W _{11(Lower)}	495.00	170.00	448724	3935911	-6.08	-30.59	18.05	-5.30	-28.98	13.42	P ₂				-2.70	-36.20	-14.60					
W _{12(Lower)}	462.00	20.00	453022	3934655	-4.28	-23.41	10.83	-3.80	-20.30	10.10	P ₃				-2.82	-37.00	-14.44					
W _{13(Lower)}	475.00	130.00	453267	3942941	-6.19	-32.54	16.98	-5.23	-30.14	11.70												
W14(Lower)	434.00	180.00	445277	3948471	-5.10	-21.42	19.38	-5.18	-21.49	19.95												
W _{15(Lower)}	431.00	130.00	442713	3952430	-6.00	-29.56	18.44	-5.67	-25.65	19.71												
W _{16(Upper)}	394.00	120.00	440817	3950748	-5.01	-40.00	0.08	-4.32	-34.00	0.56												
W _{17(Upper)}	335.00	93.00	435812	3946716	-5.93	-30.46	16.98	-5.00	-27.34	12.66												
W _{18(Upper)}	318.00	130.00	434243	3952089	-5.20	-22.00	19.60	-5.00	-20.00	20.00		W: Pumping well of groundwater										
W _{19(Upper)}	335.00	80.00	436351	3951704	-5.97	-29.80	17.96	-4.70	-26.32	11.28		S: Sampling point of Lesser Zah River										
W _{20(Upper)}	323.00	85.00	431197	3957904	-4.00	-30.77	1.23	-4.30	-30.10	4.30	5. Sampling point of Lesser Zao River											
W _{21(Lower)}	324.00	120.00	440357	3964462	-6.60	-43.62	9.18	-6.00	-40.78	7.22		P: Sampling point of runoff										
W _{22(Upper)}	292.00	70.00	428042	3959100	-4.00	-34.00	-2.00	-4.20	-34.90	-1.30				R: Ra	ainwate	er samp	le					
W _{23(Upper)}	276.00	100.00	425929	3961552	-3.90	-11.25	19.95	-3.50	-10.80	17.20												
W _{24(Lower)}	586.00	150.00	449236	3955040	-2.72	-22.19	-0.43	-2.56	-21.10	-0.62												
W _{25(Lower)}	567.00	125.00	445588	3958297	-4.70	-35.31	2.29	-4.10	-32.43	0.37	_											
Min	276.00	20.00			-6.60	-46.01	-2.00	-6.75	-43.00	-1.30	_											
Max	586.00	180.00			-2.72	-11.25	19.95	-2.56	-10.80	20.00	_											
Mean	385.00	107.76			-5.14	-29.59	11.53	-4.77	-27.94	10.18	_											
St. Dev.					1.09	7.93	7.46	1.02	7.47	6.79												

Surface water:

The ratios of ¹⁸O and ²H in surface waters have been plotted against GMWL and EMWL, where the two sampling campaigns are short-term figures 4 and 5. Although there is no continuous long-term sampling, the isotopic ratios of dry and wet periods have dependent relations. The temporal variations of δ^{18} O and δ^{2} H within two seasons are attributed to fractionation processes; i.e. temperature, evaporation and rainfall amount [2-10].

During the dry period, the ranges of δ^{18} O and δ^{2} H in the Lesser Zab River are -3.12‰ to -2.82‰ and -12.80‰ to -12.00‰ respectively. At the wet period, the water samples of runoff and Lesser Zab River have been collected simultaneously. The evaporation effect is clearly noticed in runoff samples in comparison with the Lesser Zab River table 1. The lowest and highest of δ^{18} O of Lesser Zab River are -5.30‰ and -4.87‰ respectively, while δ^{2} H extends from -30.00‰ to -28.65‰. The averages of d-excess are 11.03‰ to 11.19‰ within both periods. The δ^{18} O of runoff samples reaches to -2.40‰ while δ^{2} H decreases to -37.00‰. These remarkable disparities at both seasons and then concluded the d-excess values would be due to evaporation, fractionation processes led to variation of isotopic ratios of rains. Runoff samples have greater isotopic contents; hence the depletion processes of isotopes are less [13] figure 6.



Figure 4-Plotting ²H and ¹⁸O of surface water and groundwater at dry period versus GMWL, EMWL and LMWL



Figure 5-Plotting ²H and ¹⁸O of surface water and groundwater at wet period versus GMWL, EMWL and LMWL

Groundwater:

The isotopic content of precipitation is a fingerprint of groundwater origin. Locally groundwater samples are representatives of the aquifers by 25 wells different depth undertaken within dry and wet periods. The minimum, maximum and average of δ^{18} O are -6.60‰, -2.72‰ and -5.14‰ respectively at dry period, conversely the δ^{18} O values at wet period are -6.75‰, -2.56‰ and -4.77‰. The ratios of ²H are -46.01‰, -11.25‰ and -29.59‰ as minimum, maximum and average respectively. The wet period has minimum of δ^{2} H -43.00‰, maximum -10.80‰ and average -27.94‰ table 1. The δ^{2} H and δ^{18} O of groundwater have less variation than surface water due to direct evaporation [1-2].



Figure 6-Variation of ¹⁸O and ²H ratios in Lesser Zab River and Runoff samples at dry and wet periods

Through figures 4 and 5, signatures of the wells have been fallen into two groups during two sampling periods. The first well samples are dropped between GMWL and EMWL, whereas the second samples of wells are classified below the GMWL. Taken in consideration both of them, Meteoric Water Line of Groundwater (GWWL) has been concluded within dry and wet periods. There is no significant difference between the two periods (Equations 9 and 10).

 $\delta^2 H = 4.38 \times \delta^{18} O - 7.10$

 $\delta^2 H = 4.59 \times \delta^{18} O - 6.10$

(Dry) (9)(Wet) (10)

The weak correlations of Equations (9 and 10) confirm that there is more than one recharge source of groundwater figures 6.9 and 6.10. Generally, the similar ranges of isotope contents are noticed within both periods, except some samples, which have distinct differences of δ^2 H. Even the groundwater source is unique; the δ^2 H and δ^{18} O can change by the fractionation processes throughout their traveling from the atmosphere (liquid to/from vapor), rainwater, to groundwater and occasionally in the aquifer along flow paths due to evaporation. Clearly, the groundwater has been subjected to significant evaporation and ion exchanges. Confirmedly temporal and spatial origins of groundwater can be known in case there are not any effects on isotopic signatures. The range of d-excess is -2.00‰ to 19.95‰ within dry period while it has -1.30‰ to 20.00‰ at wet period table 1.

The wells that have higher isotopic ratios are higher values of d-excess, which mean their water suffered much more evaporation during travelling stages beginning from atmosphere till percolation or/and within flow paths of groundwater. The dry and wet periods have convergent averages of the d-excess; 11.53‰ and 10.18‰ consecutively. Even the d-excess values are closer to 10‰, the source of groundwater is LMWL during a long time.

Conclusions:

The precipitation data of δ^{18} O and δ^{2} H have been plotted along with GMWL. It is interpreted that the fractionation processes are less than what can be in rainwater samples. It has been noticed a difference

between the LMWL and GMWL, in terms of slope and intercept, and individual events will have a line different generally from the LMWL. Through isotopes, the signatures of groundwater have been fallen into three groups during two sampling periods. All well samples are dropped below the LMWL. **References:**

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