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Regular variations of the mercury concentration in natural gas

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Abstract

Direct on-line measurements of the mercury (Hg) content in natural gases by a newly developed Zeeman atomic absorption spectrometer RA-915+ have revealed a short-term variability of the Hg concentration, which has not earlier been known. The significant variability of the mercury concentration in a hydrocarbon gas was found in all of the gas wells studied. The variation magnitudes range from 10 to 80% of the average mercury content in the gas. The fluctuations have regular components with periods from few minutes to several hours and can be represented as a set of harmonics with different spectral intensity and stability in time. The most stable harmonics are characterised by intermediate frequencies with periods of 0.3–2.5 h. These 'basic' frequencies are characteristic of individual gas wells even within a single productive horizon. The remarkable features of these harmonics are the multiplicity of their periods and good agreement with phases of the Earth's own oscillations. A relatively low-frequency oscillation with a period of 25 h corresponds to a lunar tidal cycle. An oscillatory mechanism of the adsorption–desorption of mercury in a porous gas-bearing medium is assumed to be responsible for these effects.

Keywords: Zeeman atomic absorption spectrometer RA-915+; Mercury in natural gas; Regular variations

1. Introduction

The gas and oil combustion is a very significant source of mercury input in the environment (Ebinghaus et al., 1999). The typical mercury concentration in natural gas is between 1 and 200 ng/l (Shafawi et al., 1999). Mercury, being present in hydrocarbon gas, initiate corrosion of aluminium structures and catalyst poisoning, and these effects have serious implications for the oil industry (Wilhelm, 1999). Mercury extraction and purification of gases, as well as reworking the products of gas deposits, which involve mercury separating as a fairly toxic element, is very important for the environment protection (Spiric and Mashyanov, 2000). It is important even in cases when mercury is not an industrial component: the huge amounts of world annual reworking gas should be taken into account (Ozerova et al., 1999). To date, little research data have been published on the determination of Hg in natural gases. The determination of mercury reserves in gas deposits, as a rule, has been performed on the basis of a few or single

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measurements of the Hg concentration in a gas. The long-term variability of the local and average Hg content in gas pools can give rise to a significant difference in evaluation of the mercury content depending on the time of measurements. The spatial–temporal variability of the mercury concentration in hydrocarbon gases should be considered in determination of mercury resources in gas deposits and evaluation of the Hg input in the environment due to the operation of Hg-containing hydrocarbon deposits.

In this paper, new data on the long-term and regular short-term variations of the mercury concentration in natural gases are discussed.

2. Experimental technique

In this study, we used a newly developed mercury Zeeman atomic absorption spectrometer with high frequency modulation of light polarization RA-915+ (manufactured by Lumex Ltd, Russia) for direct on-line measurements of the mercury concentration in natural gases (Sholupov and Ganeyev, 1995; Ganeyev et al., 1996). The use of the Zeeman background correction and a multipath analytical cell provides high selectivity and sensitivity of measurements. As a result, the instrument allows direct determination of mercury in hydrocarbon gases due to the elimination of preliminary precipitation and collection of mercury in absorption traps. Therefore, analyses can be carried out with the ultra low detection limit (0.01 ng/l) in real time.

To perform a measurement, the spectrometer is placed near a gas well or other sampling point (gas conduit, string, separator, etc.). Gas flows continuously through the analytical cell. The gas flow rate (3–15 l/min) is controlled with a valve and is maintained constant to an accuracy of 5%. Occasionally, a simple device is mounted upstream of the instrument to separate the gas from a liquid phase (water, condensate or oil). The blank signal is regularly checked by passing the gas through a special filter with the Hg-adsorption efficiency of 98–99%. The mercury concentration is measured once per second and is processed by a computer with a simultaneous data display.

Table 1
Long-term variation of the average mercury concentration in natural gases, ng/l

Year	Deposits				
	1	2	3	4	5
1984		18.5			
1986				0.8	2.5
1987		7.3			1.5
1988			37		
1989		2.2			
1990			38	0.1	
1991	2.0[a]				
1992	0.6[a]				
1993	0.9[a]				
1995				1.7[a]	
1998		4.6			
Average	1.2	8.2	37.5	0.9	2.0
C_{max}/C_{min}	3.3	8.4	1.0	17[a]	1.6

Deposits: 1—Astrakhanskoye; 2—Mirnenskoye; 3—Oposhnya; 4—Orenburgskoye; 5—Sokolvogorskoye.

[a] Analysis of total gas arriving from the deposit to the gas plant.

3. Results

3.1. Long-term variability of the mercury concentration in natural gases

Investigations conducted over 20 years at different gas deposits in the former Soviet Union revealed the substantial variability of the average mercury concentration in investigated gas pools, which ranges from 1.6 to 17 times (Table 1).

The mercury concentrations at the same site can increase or decrease as compared to the earlier years. In some cases, a distinct reduction of the average mercury concentration in gas deposits was detected, while in other cases a rough stability of the concentrations was observed. For example, the Mirnenskoye deposit shows a distinct decrease of the average mercury concentration level from 1984 to 1989 and then a rise in 1998.

The long-term variability of the Hg concentration in individual gas wells is much greater than the average fluctuation in a whole deposit (Fig. 1). Between two measurements on a same sampling site, the concentration can vary from 18 to

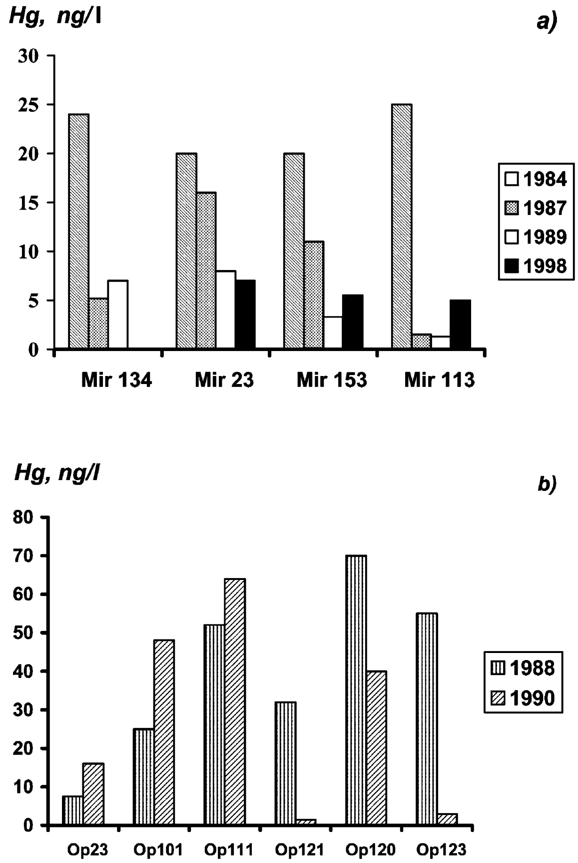

Fig. 1. Long-term variability of the Hg concentration in individual gas wells observed in different years. The data represent a set of three measurements, each 10-min long. (a) Mirnenskoye gas-condensate deposit; (b) Oposhnya gas-condensate deposit.

21 times while the mean value for the deposit remains constant (Fig. 1b).

It is well known that, during the operation of oil and natural gas deposits, concentrations of both hydrocarbons and inorganic components in extracted gases can change significantly. Unfortunately, relatively limited data, which are currently available in the literature, do not enable us to make definite conclusions about the regularities or long-term tendencies of mercury behavior in hydrocarbon pools. However, it is still possible to assume that the variability depends on many factors, such as regional-tectonic position and geologic-structural features of a deposit; storage of hydrocarbons and operation conditions, and also seismic activity in the given region. Presently, we cannot identify the dominant factors which govern the long-term tendencies of the mercury behavior in hydrocarbon pools. Nevertheless, it is obvious that the observed changes of the Hg concentration call for further study in order to understand the causes of the long-term variability and to evaluate more exactly the mercury storage in gas deposits.

The fluctuations of the Hg concentration in natural gases, which were observed in different years, bring up the necessity to study the Hg concentration stability during shorter time periods (days, hours, and minutes).

3.2. Short-term variability of the mercury concentration in natural gases

The short-term variability of the Hg concentration in hydrocarbon gases was discovered for the first time at the Oposhnya deposit, Ukraine, Poltava region (Ryzhov et al., 1999). We began a systematic study in 1998 at the Mirnenskoye deposit, Russia, Stavropol region. Both Hg-containing gas-condensate deposits studied have similar regional geological position. They are situated within the Karpinsky lineament (Dnieper-Donetsk graben and Stavropol uplift), in the areas of its intersection with deep fault zones (Ozerova et al., 1999). This ultimately results in a high mercury concentration in both deposits (Table 1).

The determination of the time dependence of the Hg concentration in these deposits involved the long-term continuous measurements ranging roughly from several hours to several days. The mercury concentration in gas wells was measured under the standard well operation conditions. The results of measurements are listed in Table 2.

The graphs of the 5-day continuous measurements at the Oposhnya (well Op-101) and Mirnenskoye (well Mir-113) deposits are depicted in Fig. 2a and Fig. 3a, respectively.

Both studied wells show noticeable changes in the Hg concentration with time. In the Oposhnya deposit, the observed value widely varies from 15 to 82 ng/l, the average concentration being 46 ng/l. Generally, the time variations in the concentration amounts to 10% of the average Hg concen-

Table 2
Average mercury concentration in natural gas and the periods of oscillations

Well	Time of measure Days.mm.yy h:min	Average Hg concentration (Min–Max) (ng/l)	Periods of oscillations T (min)	
			'Basic'	'Others'
Op-101[a]	9–13.06.90 0:00–21:00	47 (15–82)	35.4–37.3	724 (12.1 h) 16.1 11.1 0.7–8.4[b]
Mir–113[c]	16–21.08.98 15:00–12:00	4.5 (2.5–6.3)	1500 (25 h) 142	750 (12.5 h) 134 70 47
Mir-114[c]	13.08.98 13:00–18:00	2.7 (2.5–3.1)		129 55 43
Mir-153[c]	18.08.98 13:00–19:00	5.5 (4.9–7.0)	65	130 43
Mir-23[c]	19.08.98 14:00–19:00	7.2 (6.7–7.7)	33	43
Mir-152[c]	20.08.98 12:00–16:00	1.2 (1.0–1.4)		125

[a] The Oposhnya gas-condensate deposit.
[b] The oscillations are observed only in some intervals of the peaks of the Hg concentration.
[c] The Mirnenskoye gas-condensate deposit.

tration in the gas. However, these variations can sometimes reach a maximum of 80%. The average Hg concentration in the gas of the Mir-113 well at the Mirnenskoye deposit is 4.5 ng/l, and its value fluctuates with time in a range of 25–40% with respect to the average concentration.

Fig. 2b and Fig. 3b depict enlarged graphs of two characteristic time-fragments from the overall measurements. These curves show obvious regular time variations in the mercury concentration. These variations by far exceed possible analytical error; hence they represent some periodic processes, which take place in a dynamic 'well-deposit' system. It should be noted that the pressure and daily gas production did not change during our measurements.

The collected data were processed with the Fourier transformation to define regular spectral components (Fig. 2c and Fig. 3c). Relatively low-frequency oscillations with periods (T) from 12 to 25 h are observed in the spectra, as well as middle-frequency components with periods ranging from 0.3 to 2.5 h (Table 2). Relatively high-frequency components with the T values varying from 0.5 to 5 min were observed only at the Op-101 well for some intervals of the peak Hg concentration. Both periods and frequencies corresponding to these oscillations, which exhibit harmonics with a maximum spectral intensity, are further referred to as 'basic' ones. Spectral components with a low intensity or those which were not reliably identified because of the insufficient observation time are conventionally called 'other' harmonics. The periods of the basic harmonics obtained from the Fourier and spectral-time analyses are listed in Table 2.

In addition to continuous 5-day observations at the Mir-113 well, a second RA-915+ instrument was used to carry out simultaneous 3–7 h measurements at other wells of the same Cretaceous productive horizon of the Mirnenskoye deposit. Regular variation patterns were obtained at all the

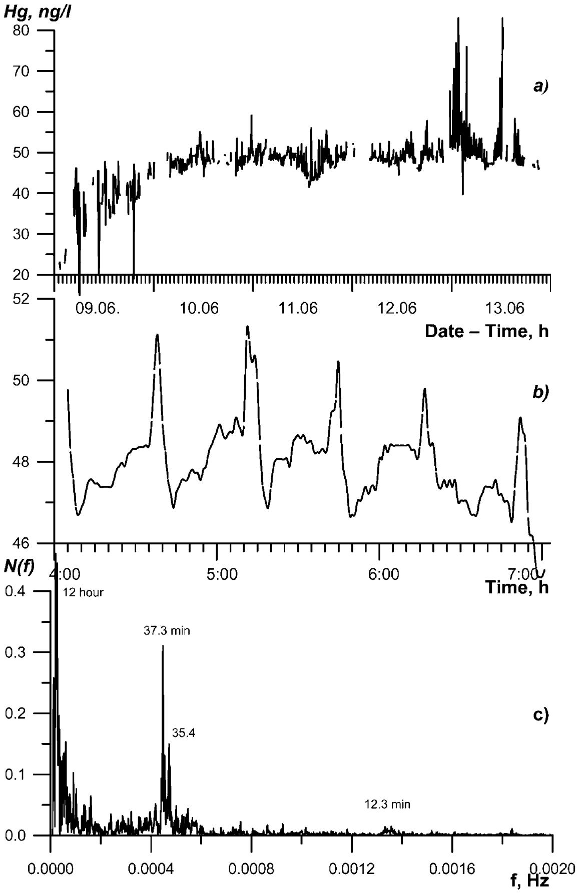

Fig. 2. Temporal variability of the mercury content in hydrocarbon gas from the Oposhnya deposit (the first observation of the regular variations). (a) Continuous measurements at the Op-101 well, June, 9–13 1990; (b) typical fragment of a record with 8.4–35.4-min regular variations; (c) Fourier-spectrum of the oscillations intensity for total data.

studied wells. Different sites of the same gas-producing layer showed different periods of the basic oscillations (Table 2), which exhibit a very interesting feature of their multiplicity: 33, 65, and 142 (134) min. For example, Fig. 4 depicts the results of simultaneous observations at the Mir-113 and Mir-153 wells, where the basic periods of 65 and 142 min were detected.

It should be pointed out that drastic changes of the operation conditions (e.g. a sudden ejection of a stream of water and gas-condensate mixture in the gas) affected both the behavior of variations and the mercury concentration measured in the hydrocarbon gas.

The 25-h variations, which match the duration of the lunar day, are revealed in the Fourier spectrum of the long-time measurements at the Mir-113 well. The tidal surface displacements at the observation points were calculated using an advanced algorithm (Mathews et al., 1997). The

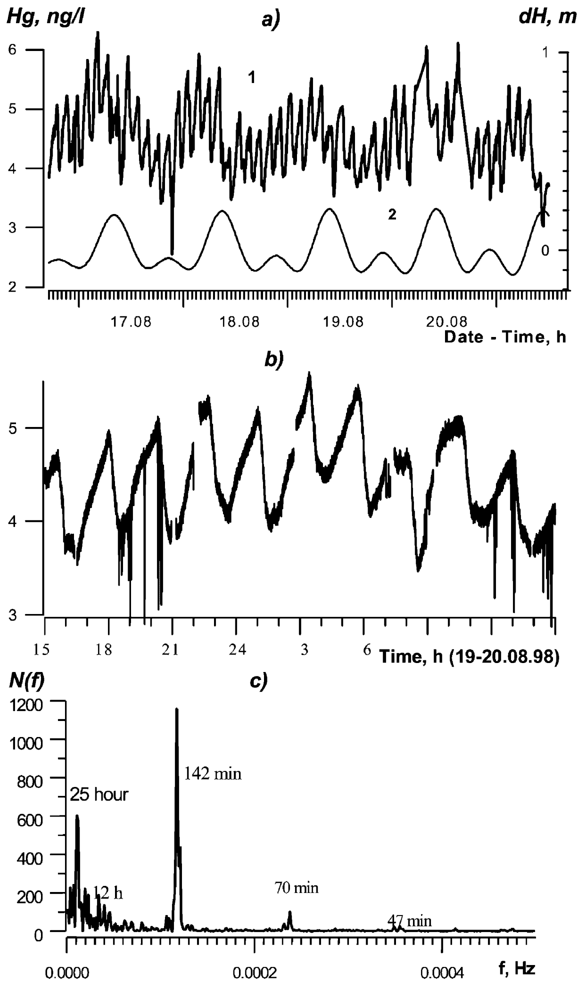

Fig. 3. Temporal variability of the mercury content in hydrocarbon gas from the Mirnenskoye deposit. (a) Continuous measurements at the Mir-113 well, August, 16–21 1998 (curve 1) and the vertical component of tidal displacement dH (curve 2); (b) typical fragment of a record with 142-min regular variations; (c) Fourier-spectrum of the oscillations intensity for total data.

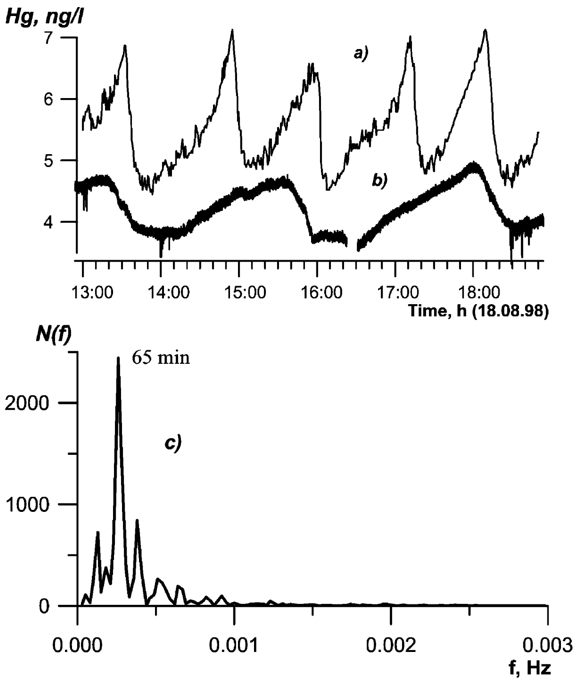

Fig. 4. Simultaneous measurements of the Hg concentration in hydrocarbon gas from the same gas-productive layer: the Mir-113 and Mir-153 wells of the Mirnenskoye deposit. August, 18 1998. (a) The Hg concentration in gas from the Mir-153 well; (b) the Hg concentration in gas from the Mir-113 well; (c) Fourier-spectrum of the oscillations intensity for the Mir-153 well (for the spectrum for the Mir-113 well see Fig. 3c).

maximum amplitudes of the vertical surface deformation (dH) amounted to 33 cm with a corresponding speed of compression and stretching of 0.44 mm/min. In Fig. 3a, one can see a good phase agreement of the measurement and calculated data: the maxima of the surface rise dH correspond to the minima of the Hg concentration in the gas flow. Increasing static load on a gas-producing layer (as the dH value decreases from a maximum to minimum) induces an increase of the mercury concentration in the gas stream and, on the contrary, a static load decrease (as dH increases) accordingly leads to reducing the concentration. Twofold amplitude changes in 25-h harmonic oscillations correspond to a 25% variation of the average concentration (approximately 15% at the Op-101 well in the Oposhnya deposit). This suggests that the dynamic sensitivity (caused by mechanical strains) of the equilibrium between vaporous and adsorbed-phase elemental mercury in heterogeneous porous media is very high.

4. Discussion

The following results have been obtained in the long-term continuous observations at two gas deposits, Oposhnya and Mirnenskoye:

1. All the studied gas wells show significant temporal variability of the Hg concentration in hydrocarbon gas under common operation conditions.
2. The fluctuations have regular components with periods from few minutes to several hours, which can be represented as a set of harmonics with different spectral intensity and stability in time.
3. The most stable harmonics have intermediate frequencies with periods of 0.3–2.5 h. These basic frequencies are characteristic of individual gas wells, even within a single productive horizon. The remarkable feature of these harmonics is the multiplicity of their periods.
4. Many-day observations revealed relatively low-frequency harmonic oscillations with a period of 25 h, which corresponds to a lunar tidal cycle.
5. The frequencies of oscillations are independent of the average mercury concentration in hydrocarbon gas.
6. The oscillation magnitudes range from 10 to 80% of the average mercury concentration in gas. These fluctuations exceed possible analytical error many times and, therefore, reflect a real periodic phenomenon caused by processes in geologic medium and a deposit–well system.

The regular variations of the Hg concentration in hydrocarbon gas can be related to a number of different interior and exterior factors. We assume that the Hg concentration in a gas flow has to respond to changes in pressure and strains inside a productive layer caused by the gas evacuation and also to the tidal deformations and external seismic fields. The mechanical strain, which is proportional to a seismic or tidal deformation wave, can stimulate mercury desorption from a solid surface and can also change the effective porosity of a host medium. This can reduce the Hg concentration and its rate of transfer from the porous space of a collector to the gas stream coming out of the operated well.

The cause of the regular variations with periods of 33–142 min is not quite clear. We suppose that, in addition to the causes mentioned above, the observed periodicity of the mercury concentration in natural gas reflects an autocycling process of the mercury adsorption–desorption that appears in a porous gas-bearing medium upon permanent gas extraction. The excellent coincidence of the curves obtained at different times and in different deposits may provide a basis for verification of the existence of the same (or similar) mechanism of oscillations. The outlines of three different characteristic fragments match one another almost exactly (Fig. 5). There is no dependence between the frequency/amplitude and shape of regular variations. All the peaks are asymmetric, exhibiting a relatively slow increase of the Hg concentration up to reaching a maximum and then a rapid decrease. The period and amplitude of an individual basic harmonic are probably most closely related to the resonance frequency of the 'layer-well' system. The tendency of the basic frequency increase in wells of the same horizon can be explained with an auto-oscillating mechanism that is caused by the increasing difference between the layer pressure and the pressure on the head of a well, as well as by increasing the gas debit. To gain better understanding of the causes of regular variations in the mercury concentration, it is necessary to collect further experimental data and to relate them to the available geological and geophysical information.

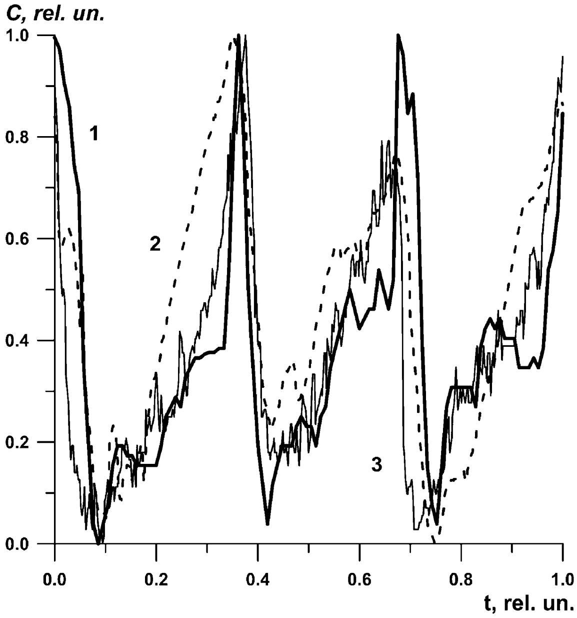

Fig. 5. Comparison of the general time dependence of the Hg concentration at different sampling points. The data are normalized to the frequency and amplitude of the variation. (a) The Oposhnya deposit, well Op-101 ($T=37$ min); (b) the Mirnenskoye deposit, well Mir-153 ($T=65$ min); (c) the Mirnenskoye deposit, well Mir-113 ($T=144$ min).

In this respect, it can be interesting to compare the obtained data with the spectral composition of a very long-period seismogravitational oscillation of the Earth (Gaulon, 1971). This can be illustrated by a comparison and good agreement between the basic oscillation periods (and their fourth harmon-

Table 3
Comparison of the observed mercury concentration variations in hydrocarbon gases with the periods of the Earth's oscillations

Periods of the mercury concentration variations in gas deposits T (min)			Periods of the Earth's own oscillations T (min) and the nearest multiplets ($_0S_n$)
$T_{\mathrm{mirnenskoye}}$	$0.25T_{\mathrm{Mirnenskoye}}$	T_{Oposhnya}	
142[a]	35.5	35.4[a]	35.56 ($_0S_3$)
65[a]	16.2	16.1	16.06 ($_0S_6$)
43	10.8	11.1	10.56 ($_0S_9$)
33[a]	8.3	8.4	8.4 ($_0S_{12}$)

[a] The values of the most stable ('basic') periods.

ics) detected at two deposits studied and the phases of the Earth's own oscillations (Table 3). Because of the limited experimental data, we restrict our consideration of such a coincidence to the regular variations of the mercury concentration in hydrocarbon gases.

5. Conclusions

The data presented here demonstrate a significant spatial–temporal variability of the mercury concentration in hydrocarbon gases. The long-term variability of the Hg concentration in the extracted gas can give rise to significant differences in the mercury storage evaluation depending on the time of measurements.

Continuous many-day observations at two gas deposits revealed a new phenomenon: the regular short-term variation of the mercury concentration in hydrocarbon gases. Generally, the time variations in the Hg concentration amount to 10% of the average Hg concentration in the gas and can sometimes reach a maximum of 80%. The Fourier analysis revealed the most stable harmonics of intermediate frequencies with periods of 0.3–2.5 h. The 25-h variations match the lunar tidal cycle. The significant amplitude changes in harmonic oscillations suggest that the dynamic sensitivity (caused by mechanical strains) of the equilibrium between vaporous and adsorbed-phase elemental mercury in the geological media is very high.

A comparison of the obtained data with the spectral composition of very long-period seismo-gravitational oscillations of the Earth show good agreement between the basic oscillation periods (and their harmonics) detected at different deposits studied and the phases of the Earth's own oscillations.

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