Impact of heat waves (HWs) on air pollution (case study for HWs episode in July-August 2010 in the Kiev city (Ukraine)

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Introduction. Kiev is the capital of Ukraine and important industrial, scientific, educational and cultural center of Eastern Europe. Kiev has a population of 3,14 million and occupies an area of more than 840 square kilometers. The biggest environmental problem in Kiev is air pollution (also called the atmosphere pollution). The overall level of air pollution in Kiev is above average in the whole Ukraine and is estimated as high. There are more than two dozen different contaminants in the air in Kiev. Most of them are sulfur dioxide, carbon monoxide, nitrogen dioxide, formaldehyde, and the usual dust.

The main sources of air pollution in Kiev are cars. In Kiev, road transport provides almost 90% of all harmful emissions into the atmosphere. Number of vehicles in the city has increased from 440 thousand units in 2000 to 830 thousand units in 2010. In the same time amount the incoming pollutants into the atmosphere from road transport increased from 160 thousand tons in 2000 to 236 thousand tons in 2010. On-road motor vehicles are one of the largest contributors to air pollution in urban environments (Franco et al., 2013; Wang et al., 2015) and thus may be a major source underlying the 3.7 million deaths per year related to air quality worldwide. Air pollution is associated with cardiovascular and respiratory diseases, and lung cancer (Kampa et al., 2008; Snizhko et al.,2010). Vehicle emissions contain a vast number of pollutants, some with toxicological relevance such as fine particulate matter ($PM_{2.5}$), ultrafine particles (<100nm diameter), carbon monoxide (CO), nitrogen oxides (NOx), and volatile organic compounds (VOCs) 10 including their secondary transformation to tropospheric ozone and particulate matter.

The increasing air pollution level significantly depends on meteorological conditions, especially on heat waves (HWs).). Direct impacts of meteorology on atmospheric chemistry are very complex. Usually, during heat wave periods air quality gets worse. Concentration of ozone (O_3), the photochemical air pollutant can rise dramatically during the periods of warm and sunny weather that is characteristic for prolonged HWs. Hot weather also tends to the increase in the concentrations of particulate matters (PM) and other pollutants. The interactions between meteorology and chemistry can be significant during strong air pollution episodes such as wild fire or dust events (Kong at al., 2014). For example, unprecedented hot and dry weather in summer 2010 caused intensive forest and peat bog fires over the vast territory of Central Russia. This very high aerosol concentration significantly changed the atmospheric gas composition, optical and radiative characteristics of aerosol (Galytska et al., 2015).

Episodes in summer with an extremely high near-surface air temperature lasting several days or longer are termed as heat waves (Robinson, 2001). Under a meteorological point of view they are generally associated with quasi-stationary anticyclonic circulation anomalies, which produce subsidence, clear skies, warm-air advection and prolonged hot conditions in the near-surface atmosphere (Fischer et al., 2007; Barriopedro et al., 2011; Shevchenko et al., 2014). HWs represent a natural hazard and have significant impacts on wellbeing (Matzarakis A. and Mayer H.,1991), efficiency and health of humans, which can lead to marked short-term increases of morbidity and mortality (Kovats and Ebi, 2006; Basu, 2009), particularly in cities, where most humans are living.

Our study of HWs in Ukraine (Shevchenko et al., 2014) for the period 1911-2011 indicate, that in contrast to other decades, the number of HW episodes was highest for almost all stations in the decade 2001–2010. For many stations, the longest HW duration occurred in the first two decades of August 2010, i.e. in the period of the extremely severe HW in Western Russia.

During July-August 2010 in Kiev were observed two HWs:1) from 14.07 to 24.07.2010 (11 days); 2) 31.07–17.08.2010 (18 days). In this study we will analyze interactions between meteorology and chemistry for second biggest HW. During second HW excess of the average daily temperature was at least 5°C; about 10 days this excess reached 8-10°C; maximal days temperature reached 38,2°C (8.08.2010).

During periods of HWs in urban areas created ideal conditions for the accumulation of a number of pollutants and formation of photochemical smog.

Air quality monitoring in the city of Kiev. The National meteorological service of Ukraine conducts air quality monitoring in Kiev. Monitoring net consist of 16 air quality stations (Fig.1).

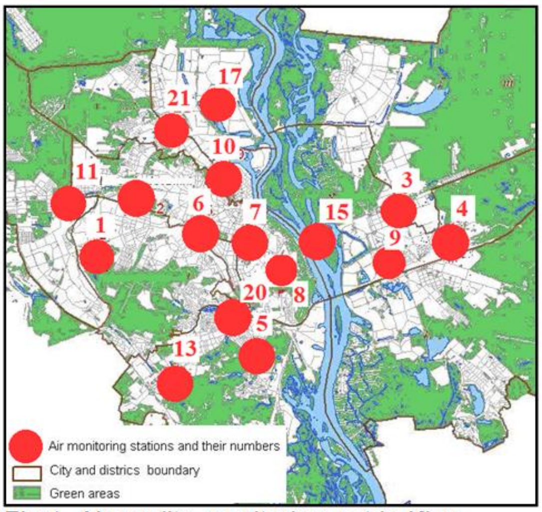

Fig.1. Air quality monitoring net in Kiev

Three stations are on the left bank of the Dnipro river (monitoring station 3, 4 and 9), station 15 is situated on the Venetian island of Dnipro river and 12 stations are situated on the right bank of the Dnipro and represents air quality in the central part of the city. Measurement of basic air pollutants makes 4 times per day (at 01, 07, 13, 19 hours).The main objectives of such measurements are to analyze any trend in ozone precursors, to check the efficiency of emission reduction strategies, to check the consistency of emission inventories and to help attribute emission sources to observed pollution concentrations. An additional aim is to support the understanding of ozone formation and precursor dispersion processes. Measurement of ozone precursor substances include nitrogen oxides (NO and NO_2), and appropriate volatile organic compounds (VOC). Monitoring program includes measurement of formaldehyde as representant of VOC.

Features of air pollution in Kiev and contents ozone precursors substances. In Kiev were detected a significant increasing in the concentration of ozone precursors during last 20 years, especially NOx (by 50%) and non-methane VOCs, for example formaldehyde (by 200%) due to the increasing number of road transport in the city. Mean annual concentration of PM_{10} after evaluating by calculation method increased by 150% for the central part of the city Kiev and 6 times exceeds European threshold value 40 µm/m^3 (Snizhko and Shevchenko, 2013).

Long-term dynamics of NO_2 and formaldehyde mean annual concentrations in the air of the Kiev city presents on Fig.2.

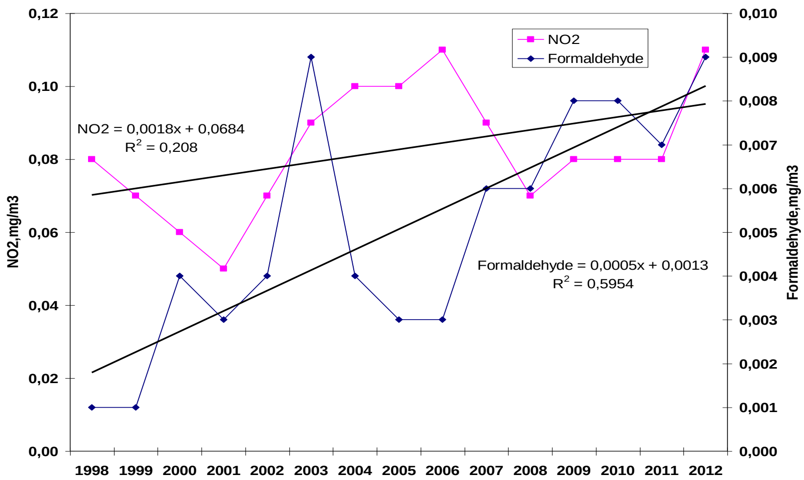

Fig.2. Long-term dynamics of NO_2 and formaldehyde mean annual concentrations in the air of the city Kiev

As we can see from Fig.2, only mean annual concentrations of formaldehyde in air have increased in last period 3 times and concentrations of NO_2 increased in 1,5-2,0 times. High concentrations of nitrogen dioxide in the air contribute to the formation of photochemical smog. During HWs periods by accelerating photochemical processes it take part as ozone-precursor in photochemical reactions. O_3 is a secondary air pollutant that is formed in the troposphere by catalytic photochemical reactions of nitrogen oxides ($NOx=NO+NO_2$) with carbon monoxide (CO), methane (CH_4) and other volatile organic compounds (VOCs).

In our previous studies (Snizhko and Shevchenko, 2011) were showed that the worst air quality in Kiev observed in central part of the city, especially on the monitoring stations 6 (Victory square) and 7 (Besarabska square). Difference in concentration of pollutants in air between this stations and stations with better air quality № 5 (Science avenue) and № 13 (Centre of Exposition) is 3-5 times.

Mean monthly concentrations of NO_2 in air of the city are relative high in warm period of year (May-September) (Table 1). This obviously can be explained by weather factors (predominance of synoptic situations that were favorable for the formation and accumulation of nitrogen dioxide in the air of the city in those months), because the structure of the emission of pollutants and their amounts are generally not undergo drastic changes in May-September.

Table 1. Concentration of NO_2 in the ambient air during warm period of the year, Kiev

Month/Year	2008	2009	2010	2011	2012
May	0,067	0,097	0,089	-	0,155
June	0,069	0,081	0,121	0,098	-
July	0,061	0,076	0,106	0,103	0,137
August	0,086	0,078	0,125	0,073	0,119
September	0,076	0,084	0,071	0,074	0,121

Table 2. The monthly frequency (min-max, %) of cases exceeding threshold of values by one-hour concentrations of NO_2 on the different monitoring stations from May to September

Station/Year	2008	2009	2010	2011	2012
5	0,0	0,0	0,0	0,0	0,0
6	0,0–6,5	0,0–4,2	2,3–50,0	0,0–20,8	12,0–62,5
7	0,0–24,0	10,9–13,5	1,9–40,0	0,0–22,9	25,0–65,4
11	1,0–6,5	0,0–10,4	0,0–24,0	0,0–9,6	6,7–58,3
13	0,0	0,0–1,9	0,0–4,0	0,0	0,0–1,9
21	0,0–4,0	0,0–14,6	3,7– 9,1	0,0–16,7	7,7–58,3

This table shows that maximal frequency of cases exceeding the NO_2 threshold values were observed on the monitoring stations 6 (Victory square) and № 7 (Besarabska square) again. Maximal frequency were observed in 2010 on the station 6 (50%) and in 2012 on the station 6, 7, 11 and 21 (58,3–65,4%).

Mean formaldehyde concentrations during warm period in air of the city are presented in Table 3.

Table 3. Mean formaldehyde concentrations during warm period (May-September) at different monitoring stations in Kiev

Year	Air pollution monitoring stations									
	1	2	3	6	7	8	9	11	17	21
2010	0,011	0,012	0,011	0,012	0,014	0,011	0,011	0,012	0,012	0,013
2011	0,009	0,011	0,011	0,010	0,012	0,009	0,010	0,011	0,010	0,010
2012	0,012	0,014	0,012	0,014	0,017	0,012	0,013	0,014	0,013	0,015

Highest concentrations of formaldehyde were observed on the Victory square (station 6) and Besarabska square (station 7). Due to constant increasing of formaldehyde air pollution its concentration in 2010 was three times higher than the its threshold value (0,003 mg/m^3).

The content of formaldehyde in the air of Kyiv mainly determined by two main sources - emissions from motor vehicles and the incoming from photochemical processes in the ground layer of atmosphere in conditions of the high level of air pollution and high concentration of precursors of photochemical reaction such NO_2 and formaldehyde.

Recent years were observed a 100% exceeding of daily concentrations of formaldehyde on about all monitoring cities. This reflects not only the high level of pollution of formaldehyde air pollution, but also the intensity of photochemical processes and serious danger to public health.

Interactions between meteorology and chemistry during heat waves episode in July-August 2010. During HWs periods in urban areas created ideal conditions for the accumulation of a number of pollutants and formation of photochemical smog. First, temperature increases favoured the chemical production of ozone in the troposphere. Second, low atmospheric humidity reduced ozone destruction, as well as the production of the hydroxyl radical, which destroys several air pollutants, including those which are ozone precursors. Third, the vegetation was affected by high temperature and the lack of precipitation, which led to a substantial reduction in the removal by dry deposition to the Earth's surface of ozone and other compounds.

We chose two stations in the city center with high level of air pollution to study interactions between meteorology and chemistry during HWs. Next, we will consider the features of pollution processes using observations at station 6 (Victory square) and stations 7 (Besarabska square) during period of biggest HW in 2010 (from 31.07 to 17.08.2010).

Fig. 3 shows features of temporal dynamics of main ozone precursors (NO_2 and formaldehyde) during HW in Kiev from 31.07 to 17.08.2010. All plots shows sufficient increasing both substances in period of HW. But character of change concentrations of NO_2 and formaldehyde is a bit different. Content of formaldehyde increases with increasing temperature and reaches a maximum in the hottest days of this period. Content of NO_2 first raised at the beginning of the HW and then slightly decreases. Moreover, its content is higher compared to the period before and after the heat wave. This behavior of NO_2 may be connected with his participation in photochemical processes

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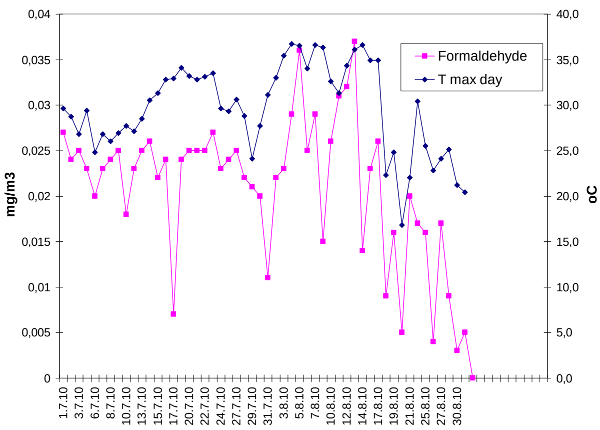
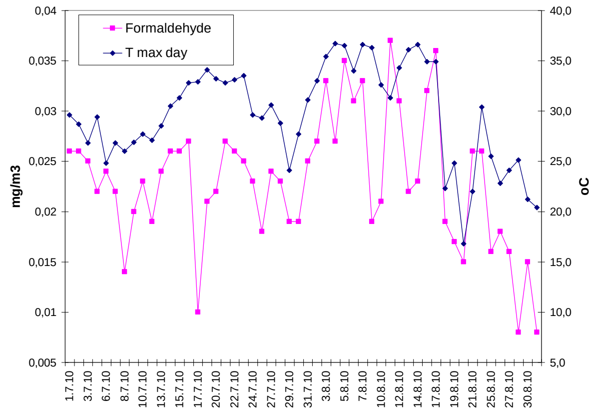
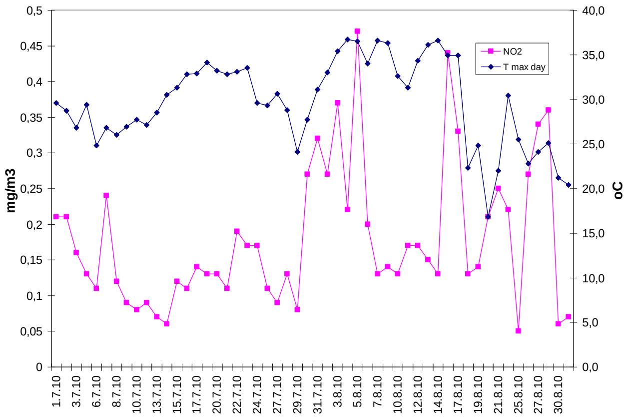


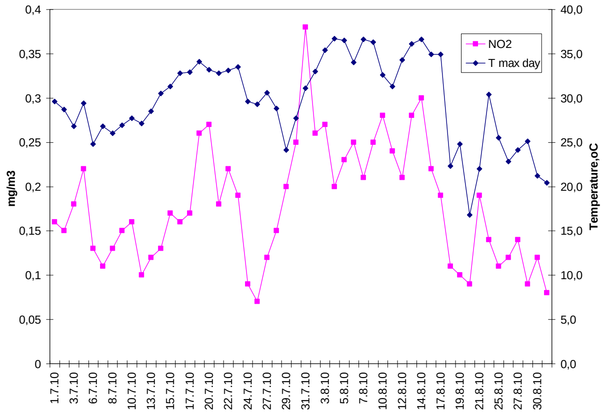
Formaldehyde, Station 6



Formaldehyde, Station 7



NO_2, Station 6



NO_2, Station 7

Fig. 3. Temporal interaction between T max day and daily NO2/ Formaldehyde concentrations

The accumulation in the urban atmosphere during HW period significant amount of NO_2, as main precursor of photochemical smog, led to production of enormous amount of formaldehyde. Maximal concentration of formaldehyde reached 0,037 mg/m^3 on 8 August 2010. This amount exceeds 12 times of threshold values and exceeds 2 times pre-HW's level of concentration. At the same day concentration of aerosols reached maximal level too (AOT=1,31) and exceeds 4 times of its pre-HW's level. Concentration of NO_2 was changed from 0,2 to 0,25 mg/m^3, its sufficient increasing during HW period was not detected. During HWs periods by accelerating photochemical processes it take part as ozone-precursor in photochemical reactions. After HW period concentration of both pollutants has decreasing very sufficient (Table 4, 5).

Table 4. Comparison of formaldehyde concentration in air during HW period and after HW period

Period	Air monitoring station								
	1	2	3	6	7	8	9	11	17
HW period (31.07-17.08)	0,025	0,025	0,028	0,026	0,029	0,025	0,023	0,027	0,026
Post- HW period (18.08-31.08)	0,009	0,010	0,011	0,011	0,017	0,012	0,010	0,014	0,012

Table 5. Comparison of NO_2 concentration in air during HW period and after HW period

Period	Air monitoring station								
	1	2	3	6	7	8	9	11	17
HW period (31.07-17.08)	0,08	0,11	-	0,06	0,24	0,24	0,17	0,18	0,25
Post- HW period (18.08-31.08)	0,07	0,08	-	0,03	0,19	0,12	0,09	0,09	0,09

To estimate the impact of HW on air pollution we have performed a comprehensive analysis of climatic characteristics and some air pollutants, in particular NO_2, formaldehyde and AOT-index (Aerosol Optical Thickness). Statistical analysis shoved high positive correlation between temperature indexes and concentrations of pollutants. Significant values coefficients of correlations reached for connection between Tmax daily and concentrations of formaldehyde 0,56; for Tmax daily and NO_2 – 0,62. Enough significant coefficient of correlations were investigated for the relationships of formaldehyde and NO_2 concentration (r=0,50). It can means that oscillation of both substances in the time determined by the same dominant meteorological factor. Index of T max daily may be a good descriptor of coupled impact of meteorological factor on ozone formation processes in the ground level layer of air. Impact of temperature on formaldehyde formation confirms a significant value coefficients of correlations between Tmax day and formaldehyde concentration (r=0,588). This relationship was approximated by linear regression equation (Fig. 4).

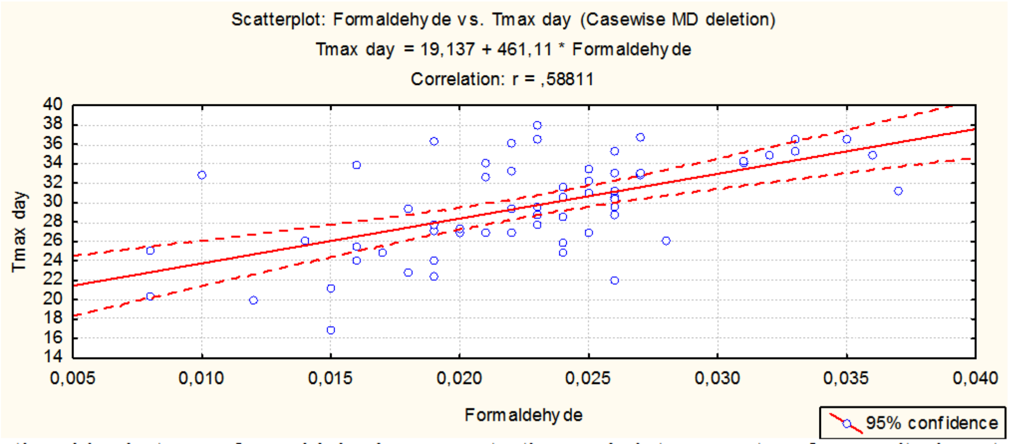


Fig.4. Relationships between formaldehyde concentration and air temperature for monitoring station 6

The above data indicate that concentration of formaldehyde depend on temperature and concentration of NO_2. Using the PC-Program “Statistica” we have calculated the relationship between formaldehyde accumulation and leading ozone precursor NO_2 and air temperature and have got relative good approximation of this relationship in form of 3D Contour Plot (Fig. 5).

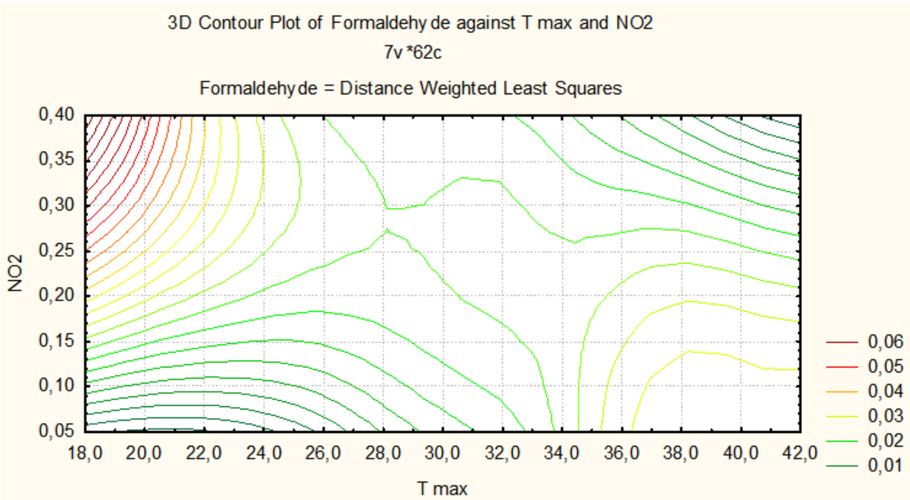


Fig.5. Graphical approximation (3D Contour Plot) of relationship between formaldehyde, NO_2 and air temperature

It presents distribution of probably formaldehyde concentration in bright range of air temperature (T max daily) from 18,0 to 42,0°C and NO_2 concentration from 0,05 to 0,40 mg/m^3. Fig. 6 shows that probability of formation highest concentrations of formaldehyde is possible in two cases:

- highest concentrations of NO_2 in range 0,20-0,40 mg/m^3 and relatively low for summer HW episode temperature in range from 18,0 to 23,0 °C;
- relatively low concentrations of NO_2 in range 0,05-0,20 mg/m^3 and very height temperature – 35,0–42,0°C.

For approximation relationship between formaldehyde, NO_2 and air temperature we have calculated an equation of multiple linear regression:

Formaldehyde (mg/m^3) = 0,001577+0,011329 NO_2 (mg/m^3)+0,000648 T max day (°C).

Results of retrospective forecast calculation using this equation and monitoring dates from station 6 shows satisfactory results (Fig. 6). Mean relative error of forecast for this case makes up 37%.

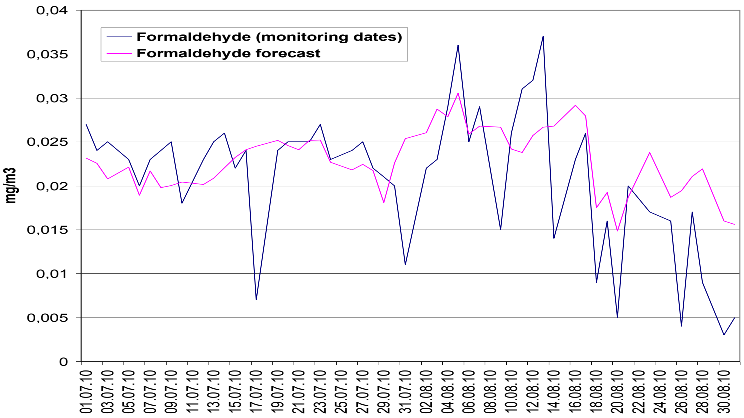


Fig. 6. Comparison of retrospective forecast for formaldehyde concentration with monitoring dates from station 6 (Besarabska square – centre of Kiev)

This equation can use as statistical model for short-time expert assessment of formaldehyde accumulation in urban air during HW cases if not available a more modern numerical forecast models.

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