Article

Impact of hydrocarbon emissions from oil and gas deposits on δ13С variability in pine tree rings from Tatarstan Republic

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**Abstract:** Human-caused anthropogenic greenhouse emissions impact climate globally. In this pilot study, we aim to reveal impact of oil and gas emissions from local deposits in the regime of their natural degradation and development as well as their impact on eco-physiological changes of pine forest in Tatarstan Republic, Russia over the past century. We performed stable carbon isotope analysis in pine tree-rings (δ13Cptrw) to reveal impact of oil and gas emissions from the giant oil field reservoirs located in Leninogorsk region (UVRT) and natural reserve site in Raifa. Our results show decreasing δ13Cptrw at UVRT in 1943, when oil extraction was started and in 1970, when it is reached the maximum production. We found that δ13Cptrw from UVRT indicates on developing unfavourable drier conditions and suppressed tree growth caused by both human-induced oil and deposit infrastructure and natural processes compared to undisturbed Raifa. A 5-year running correlation analysis showed significant difference between sites in 1965 over the period 1930 to 2021. The δ13Cptrw from Raifa are more negative compared to UVRT, which can be explained by higher forest sensitivity to human-induced impact. From ecophysiological point of view decreasing intercellular to ambient CO2 concentration at the leaf level and increasing intrinsic water use efficiency along with decreasing tree-ring width at UVRT (1970-2021) indicate on developing of drought conditions.

**Keywords:** CO2; CH4; δ13С in tree-ring wood; soil; iWUE; climate;

1. Introduction

Accelerated development of energy resources around the world has significantly increased forest change associated with oil and gas activities, leading to both carbon dioxide and methane emissions. The impacts of these anthropogenic indirect greenhouse gases (GHG) play a significant role on forest ecosystems at the regional and global scales [1].

The GHG attributed up to 65 % to human activities [2], including hydrocarbon emissions from the oil and gas infrastructures [3] causing a global average air temperature increases by 1.4°C [4]. Moreover, the extraction and refining of oil produces about 48% of hydrocarbons and 44% of carbon monoxide [5], which can significantly impact the environment. Toxic contamination of soil can lead to reduction air exchange in the soil hindering the water flow into the soil compared to clean natural soils. Water shortage in the soil lead to soil fertility and microbial activity impacting forest ecosystem negatively.

Additionally local oil and gas production delivers up to 90% of hydrocarbons, which contribute to the global GHG emissions [6]. Due to intensive development of oil and gas depositions, oil and oil products refining the problem of their emissions locally and globally impacting the environment and humans’ health.

Recent climate change and drought-induced trees mortality affect forest ecosystems worldwide [7]. It is well known that forest soils and permafrost are important sink for atmospheric methane emissions, where a GHG is contributing roughly 20% to the global warming [8-9]. Soil microorganisms remove about 30 million tons of GHG from the atmosphere annually, which is 6 - 10% of its annual flow [10]. Living and dead trees have the potential to be CH4 sources or sinks or both [9]. Different tree species have different effects on the activity of CH4 oxidation in the soil - the highest is noted under *Pinus cembra* L. (27.68 mg kg-1) in Europe, in *Larix sibirica* Led. (7.98 mg kg-1), *Pinus sylvestris* L. (4.96 mg kg-1) and the lowest - in spruce (4.62 mg kg-1) forest [10].

The carbon atoms fixed in tree-ring width originated from the atmospheric carbon dioxide to which the tree’s canopy is exposed [9].During photosynthesis several fractionation steps take place, first when CO2 from the atmosphere (ca) diffuses into the leaf (needle) intercellular spaces (ci), and second during CO2 fixation by the enzyme Rubisco [9]. The opening and closure of stomata (gs) determines the water control. Under warm and dry conditions trees respond to limited water resources by reducing stomatal conductance (gs), resulting in decreasing CO2 uptake and biomass production, in reduced intercellular CO2 concentration (ci) [11]. Changes in the assimilation rate of the needles will therefore influence the intercellular CO2 concentration (ci) through changes of the rate at which the CO2 is utilized to form sugars and an increase or decrease in stomatal conductance will affect the rate at which this internal CO2 (ci) can be replenished [9]. Trees discriminate more strongly against 13C under conditions of high (ci), when stomata are relatively wide open, or photosynthesis is low [11]. Under increasing CO2 concentration, the water vapor exchange between the needles and the ambient air (ca) is reduced and stomatal conductance decreases [13-14]. The carbon isotopic ratio (13C/12C or δ13C) in tree rings reflects signals of water availability and air humidity as a result of the impact of climate on photosynthesis. Atmospheric CO2 is well mixed, but the sub-canopy air space can become depleted in 13C due to inputs from soil and plant interaction. Tree growth is influenced by many factors such as solar irradiance, ambient air temperature, precipitation, air humidity, soil and ground water, nutrient availability as well as water. The heavier stable carbon isotope (13C) in tree rings is modulated by environmental parameters like temperature and moisture regime changes due to fractionation processes during CO2 uptake as well as those related to land management, disturbances like insects [7, 11-12,14-16]. Photosynthetic limitations of intrinsic Water Use Efficiency ---(iWUE) can be an indicator for oil refinery in case of increase, which correspond with NOx pollution [17] and moisture changes, reducing climate sensitivity [18]. If trees uptake a significant amount of hydrocarbon emitted from the gas and oil deposits, then we suggest that tree-ring δ13C should also get more negative values.

Data on hydrocarbon (HC) production are available for the study area, however, it is not possible to estimate how much hydrocarbons are released from gas and oil deposits into the air, surface water, groundwater and soil. The HC emissions most likely occur from the subsurface prior the oil and gas deposit development. It was a more or less constant flow, for hundreds of thousands and millions of years, which could change only in case of any events like earthquakes [19]. But after the beginning of field development, the equilibrium established during a long geological time was broken that could lead to an increase in the flow of hydrocarbons both from natural fractures and faults and due to losses during production and transportation. In the first stage of extraction, oil is extracted through natural processes. As a result, it is replaced by water. If the pressure in the reservoir does not allow oil to come to the surface, then special pumps are used to extract it. Later, secondary methods are used to extract oil. It is carried out by introducing liquids and gases into oil-bearing formations to provide the necessary amount of energy to extract oil from the earth's bowels [20]. At this stage of production, the natural state of the reservoirs is disturbed and a significant emission of hydrocarbons into the air, water and soil is possible. When using the hydraulic fracturing method, HC emissions can be very large, comparable to other global sources of greenhouse gases [21]. A large increase in U.S. methaneemissions over the past decade inferred from satellite data and surface observations [22].

In the Romashkinskoye UVRT field, the hydraulic fracturing method was not used, but there could also have been noticeable HC emission during the production. Methods for assessing hidden HC emission during oil field development were not developed. Usually, only accidents in which a large volume of HC is released into soil or water are evaluated.

In this study, we hypothesized that active use of local oil and gas deposit infrastructure can lead to additional emission of CH4 and CO2 into the atmosphere, which can be recorded in trees growing close to the oil and gas deposit site.

To test this hypothesis, we developed new tree-ring δ13C in pine wood chronologies from oil and gas deposits (UVRT) and for the control natural reserve Raifa (Raifa) site to reveal impact of Romashkinskoye oil and gas deposit site on pine forest environment.

2. Materials and Methods

2.1. Study sites

Study sites are located in the Republic of Tatarstan within 54-55° N and -49-52° E, Russian Federation. We investigated two sites: UVRT - the oil and gas deposit infrastructure (UVRT) site near to Romashkinskoye deposit industrial site and Raifa – a control natural reserve site, which is located 250 km away from the UVRT (Figure 1a). The territory is located on the southern border of the southern taiga natural zone in the Volga-Vyatka high-plain complex of dark coniferous-broad-leaved forests [19].

The Romashkinskoye UVRT oil and gas deposit site Almetyevsk is located 54° N, 52° E, which is 15 km away from Almetyevsk city in the northwestern part of the Bugulma plateau, confined to the South Tatar (Almetyevsk) arch at 200-210 m asl (Figure 1a). Geological oil reserves are 5 billion tons, while proved and recoverable reserves - 3 billion tons. Exploratory drilling was started in 1943 [26-27], while in 1948 a thick Devonian formation was discovered. Intensive development and exploitation were started in 1953. At present the Romashkinskoye field is one of the largest oil fields in the world. More than 400 deposits have been identified; the main ones in terms of size: oil deposits of the Devonian terrigenous complex in the Kynovsko-Pashy sediments, this is about 70% of the explored reserves. Reserves replenishment: commercial oil reserves are growing, although cumulative production is also growing and already exceeds previously approved reserves. Depletion of sediments of the Pashinsky horizon of the Romashkinskoye field is regularly estimated at more than 85%. It is announced that residual oil reserves are concentrated in undeveloped low-permeability reservoirs. Then petrophysical works, hydrodynamic studies, seismic exploration are carried out, and the reserves are replenished. The composition of the Kynovsko-Pashy sediments indicates that anomalous zones of light oil from the Zhivet complex flowed into the wells. The Zhivetsky complex is represented by sandstones, siltstones and clays with thin interlayers of marls and limestones, and is divided into Afoninsky and Starooskolsky horizons [26].

The relief of the study site is characterised as a flat with small hills. Dry forest dominated by pine (*Pinus sylvestris* L.) (Figure 1b). The herbage is dominated by ground reedgrass, sedges and various steppe plant species. The soils are dry sod-podzol soils on sandy and sandy loam sediments.

The Raifa natural reserve (control) site 55° N, 49° E (Figure 1a) is represented by pine trees as the main dominant species (*Pinus sylvestris* L.) (Figure 2c), while rarely spruce and birch (green-moss pine forest). Pine trees (*Pinus sylvestris* L.) can reach up to 150 years. The forest stand encounters single species of *Betula pendula* Roth., *Picea* *fennica* (Regel) Kom. The understory is sparse, represented by *Euonymus verrucosus* Scop., *Tillia cordata* Mill. Dominants of the herbaceous layer are *Calamagrostis epigejos* (L.) Roth and *Convallaria majalis* L. The soil is soddy-podzolic on sandy and sandy loam deposits of the third floodplain terrace of the Volga River [17].

2.2. Local weather station observations

The climate of the region is continental with cold winters and warm summers. According to the local Kasan weather station (55° N, 49° E) average annual temperature is 5.2°С, January average temperature reaches -10.4°С, July average temperature is 20.8°С for the period from 1970 to 2021. Average snow depth in winter reaches up to 40 cm. Sum of precipitation is 584 mm per year. Maximum precipitation falls in July up to 70 mm, minimum is recorded in March up to 33 mm according to the average monthly data from Russian Research Institute of Hydrometeorological Information – World Data Center [18] for the period from 1970 to 2021.

2.3. Sampling

Tree core sampling from five dominant pine trees (*Pinus sylvestris* L.) was carried out in July 2022 at each study location (UVRT and Raifa)according to the method adopted in earlier dendrochronological studies [19]. Pine tree cores were collected at a height of 1.3 m at the breast hight on the south- and north- side of the tree from visually healthy, without double crown and not damaged living *Pinus sylvestris* L. trees using Pressler increment borer (Figure 1b,c). All tree cores were packaged in the metal foil and placed in a hard tube for transportation to the stable isotope laboratory.

Soil samples were collected in February-March 2023 using a soil drill borer. The depth of sampling ranged from 1.0 to 1.5 m . Soil samples were placed in a glass container immediately after extraction from the pits, filled with salt solution and hermetically sealed.

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| (**a**) | |
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| (**b**) | (**c**) |
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**Figure 1.** Schematic map location (**a**) and photos from (**b**) oil and gas deposits infrastructure UVRT (red circle) and (**c**) natural reserve Raifa (green circle) sites. Averaged numbers of the δ13C atmospheric CO2 [25] andδ13Cptrw are presented for the period from 1930 to 2021. The δ13C CO2 and δ13C CH4 are presented for the year of 2023 with schematic interaction of water evaporation and CH4 and CO2 soil-atmosphere-plant exchange.

2.4. Tree-ring width and stable isotope analyses

Tree-ring widths (TRW) were measured for the UVRT site for the period from 1925 to 2022 and for Raifa for the period 1887 to 2021 using a Lintab-6 with the TSAPWin software package [20]. The quality of the cross-dating chronologies was assessed by using the Cofecha software [21-22]. After that each annual tree-ring was split using a sharp BA-170P NT blade under a Leica M50 microscope.

For the stable carbon isotope analysis, each annual tree-ring sample for each year separately was packed ca. 200 µg into capsule. All measurements for each sample were repeated three times. IAEA standards were used as a reference sample for control: USGS-40 and IAEA-CH-7 with known carbon isotopic ratios.

Stable carbon isotope measurements in wood samples were performed for each tree and each year separately using a Delta V Plus isotope mass spectrometer (Thermo Fisher Scientific, Germany) via a Flash HT Plus in constant flow mode at the Kasan Federal University. Tree-ring δ13C in wood chronologies were corrected according to δ13C atmospheric CO2 for both study sites.

The δ13C CO2 and δ13C CH4 in soil samples were analysed for both sites using Delta V Plus (Thermo Fisher Scientific, Germany, SN08893D). Gas samples were separated and prepared using a TRACE 1310 gas chromatography-mass spectrometer (ThermoFisher Scientific, Germany, 713101387) coupled with an ISQ quadrupole mass detector (ThermoFisher Scientific, USA) connected to the isotope mass spectrometer via a GC Isolink interface unit. Gas sample was injected automatically by means of the TriPlus RSH autosampler (CTC Analytica AG, Switzerland) from the vial with gas with a gas-tight syringe and introduced into the chromatograph evaporator, the syringe was purged with pure helium before sampling. The volume of the injected sample varied from 0.1 mL to 2.5 mL depending on the content of the target gases in the sample. Two chromatographic columns were used for complete separation of methane, carbon dioxide, and air group gases (which interfere with the determination of the carbon isotopic ratio due to interference with nitrogen oxides). The results were processed using the “Isodat” data processing program [25].

The stable carbon isotopic ratio (13C/12C) is typically expressed in delta notation as (δ13C) (Equation 1), which is the relative deviation of the ratio in the organic sample (*R* sample) from that of an internationally accepted standard (*R* standard), Vienna Pee Dee Belemnite (VPDB).

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| δsample = (Rsample – Rstandard – 1)\*1000 (1) | 111(1) |  | (1) |

2.5. CO2 and greenhouse gas emissions (GHG)

Correction of raw tree-ring δ13C is necessary because the combustion of fossil fuels and biomass and land-use changes have resulted in a decrease in δ13C of the atmospheric CO2 over the last 150 years. Changes in the isotopic ratio of atmospheric CO2 are directly reflected in the isotopic ratios of the products of photosynthesis. Calculating the differences for each year to the pre-industrial value (1850) for δ13C of atmospheric CO2 obtained from ice cores and direct atmospheric measurements at the Mauna Loa Observatory, Hawaii [23; https://gml.noaa.gov/ccgg/trends/] we subtracted these differences from the raw isotope series for δ13C values for each year. Because isotope fractionation is additive, this completely removes the trend due to decreasing atmospheric δ13C from fossil fuel emissions and land-use changes.

Local data from the oil extraction and cumulative oil production from the gas and deposite UVRT site are available for the period 1943 to 2021 [26] for comparison with our newly developed δ13Cptrw from UVRT and controlled natural reserve Raifa site.

Global oil and gas emissions data from Russia and globally [6] were used for regression analysis with δ13Cptrw from both UVRT and Raifa sites.

2.6. Relation to intrinsic water-use efficiency (iWUE)

The calculation of intrinsic water-use efficiency (iWUE) was based on the Equations (2) and (3) described in detail by Saurer and Siegwolf [21] and Saurer and Voelker [23].

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| iWUE = (ca-ci)/1.6 | (2) |

where ca— is the ambient CO2 concentration, ci – is the intercellular CO2 concentration, and 1.6 is the ratio of diffusivities of water and CO2 in the air.

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| ci=ca • ((δ13Cair-δ13Cplant-4.4)/(27-4.4)) | (3) |

while δ13Cplant—uncorrected tree-ring δ13C measurements in pine wood relative to the δ13C atmospheric CO2; the δ13Ca—data is available from <https://www.esrl.noaa.gov/gmd/outreach/isotopes/c13tellsus.html> (accessed on 22 March 2023). Diffusion through the stomata is described as (a = 4.4‰), b is the discrimination associated with carboxylation (b = 27‰).

2.6. Statistical analysis

The statistical analysis was performed in the STATISTICA Ultimate Academic 13 RUS / EN Rus for Window). The mean, minimum, maximum values, standard deviation (SD), Pearson correlation coefficients were calculated for stable carbon isotope chronologies from both study sites. A 5-year running correlation analysis was performed between δ13Cptrw from UVRT and Raifa site to reveal a breakpoint and differences between control and oil and deposit sites. Stable carbon isotope chronologies for both study sites were detrended using time series forecasting analysis with the “no trend” function. Multiple regression analysis was performed between climate parameters, gas and oil emissions and δ13Cptrw

To reduce impact of trends in climatic and comparative analyses we use detrended stable isotope chronologies. The level of statistical significance is expressed as a *P-value* ≤ 0.05. Multiple regression analysis was performed between climate parameters, local and global gas and oil emissions versus δ13Cptrw. D**ependent variable was associated with** δ13Cptrw**, while independent variables were local and global oil gas emissions. Bivariant regression plots were computed.**

The iWUE data were smoothed by a 11-year Hamming window [24] to reveal low-frequency variations and to compare long-term trends between study sites.

2.7. Spatial climate patterns

Spatial correlation gridded maps were computed within 50-60°N, 40-55°E; *P < 0.01* between June-July-August (JJA) evapotranspiration, differences between maximal und minimal air temperature (Tmax-min), precipitation, and cloud fraction available at the KNMI Climate Explorer https://climexp.knmi.nl/ (accessed date on 29 March 2023) and detrended tree-ring δ13Cpwc from UVRT site for the period 1980-2020. The level of significance is expressed in percent (*P < 10 %*).

3. Results

3.1. Stable carbon isotopes in wood vs. oil and gas emissions

Stable carbon isotope chronologies were developed for UVRT and Raifa sites based on five individual trees for each study site for the common period from 1930 to 2021 (Figure 2a).

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| (**a**) | (**b**) |
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| (**c**) |  |

**Figure 2.** Raw and correctedaccording to δ13C of atmospheric CO2 [29] tree-ring δ13C in pine wood chronologies from UVRT (red colour) and Raifa (blue colour) sites versus δ13C atmospheric CO2 (black) from 1930 to 2021 (**a**). A 5-year window running correlation between δ13Cptrw from UVRT and Raifa sites. The break point year is represented as the dotted line in 1965 (**b**). Oil extraction and cumulative oil production from UVRT oil and gas deposit site for the period from 1943 to 2022 in comparison with δ13Cptrw from UVRT and Raifa [19] (**c**).

The mean δ13C value is more negative for Raifa (-23.6‰) compared to UVRT (-22.3‰). Standard deviation (SD) is higher for the UVRT site (1.2) compared to Raifa (0.8). Maximum and minimum values are more negative for Raifa (max -21.5‰, min -25.4%) compared to UVRT (max -19.7‰, min -24.3‰). The δ13C from Raifa showed significant correlation with UVRT (r = 0.89, p < 0.001). Moreover, we found more negative values for both δ13C CO2 andδ13C CH4 in soil samples from Raifa site (-19.3 ‰ and -64.4 ‰) compared to UVRT (-12.4 and -51.1 ‰), respectively.

A 5-year running correlation analysis between δ13Cptrw from UVRT and Raifa (Figure 2b) showed significant difference in the year of 1965, showing negative correlation (r = -0.38; p < 0.05) over the studied period 1930-2020. During other subperiods positive correlations were revealed.

The oil and gas extraction from the deposits started in 1943 and reached maximum in 1970 (Figure 2c), which correspond with decreasing δ13C values from both study sites with the most pronounced decrease for Raifa natural reserve site (Figure 2a).

Regression analysis showed significant relationships between local oil extraction and detrended stable carbon isotope chronologies for UVRT and Raifa sites (r2 = 0.14 and r2 = 0.04; p<0.05), respectively (Figure 3ab), with higher correlation for the gas and oil deposit UVRT site only.

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| (**a**) | (**b**) |
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| (**c**) | (**d**) |
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| (**e**) | (**f)** |

**Figure 3.** Detrended tree-ring δ13C from the UVRT (left panel) and Raifa (right panel) sites versus detrended local oil extraction [19] (**a-b**), global oil (**c-d**) and gas (**e-f**) [6] emissions for the period 1943 to 2021. Confidential interval is 0.95, *P < 0.05*.

The global oil and gas emissions correlate significantly with tree-ring δ13Cptrw for UVRT (r2 = 0.13; r2 = 0.31) (Figure 3c,e) and for Raifa (r2 = 0.09; r2 = 0.30), P < 0.05, respectively (Figure 3d,f).

3.2. Intrinsic water use efficiency (iWUE) versus tree-ring width and tree-ring δ13C

Earlier 1930s tree-ring width index (TRWi) chronology form UVRT shows lower mean values (1.42 mm) compared to Raifa site for TRW (1.55 mm), respectively. However, starting form 1960s tree-ring width index form Raifa showed higher values, compared to supressed UVRT site (Figure 4a).

Intercellular CO2 concentration (ci) showed higher offset between two sites starting from 1965 (Figure 4b) with higher ci for Raifa site. Strong decreasing ci/ca trend with lower values (Figure 4c) and continuous increase of iWUE (Figure 4d) were revealed for UVRT site. Both UVRT and Raifa showed similar increasing trends from 1930 towards 2020 (Figure 4d).

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| (**a**) | (**b**) |
|  |  |
| (**c)** | (**d**) |

**Figure 4.** Averaged tree-ring index chronologies (**a**), intercellular CO2 concentration (ci) (**b**) and intercellular CO2 concentration versus ambient CO2 concentration (ci/ca) from Raifa versus oil and gas reservoirs UVRT site (**c**). Intrinsic Water Use Efficiency (iWUE) calculated for both Raifa and UVRT study sites (**d**).

3.3. Impact of local environmental parameters on tree-ring δ13C variability

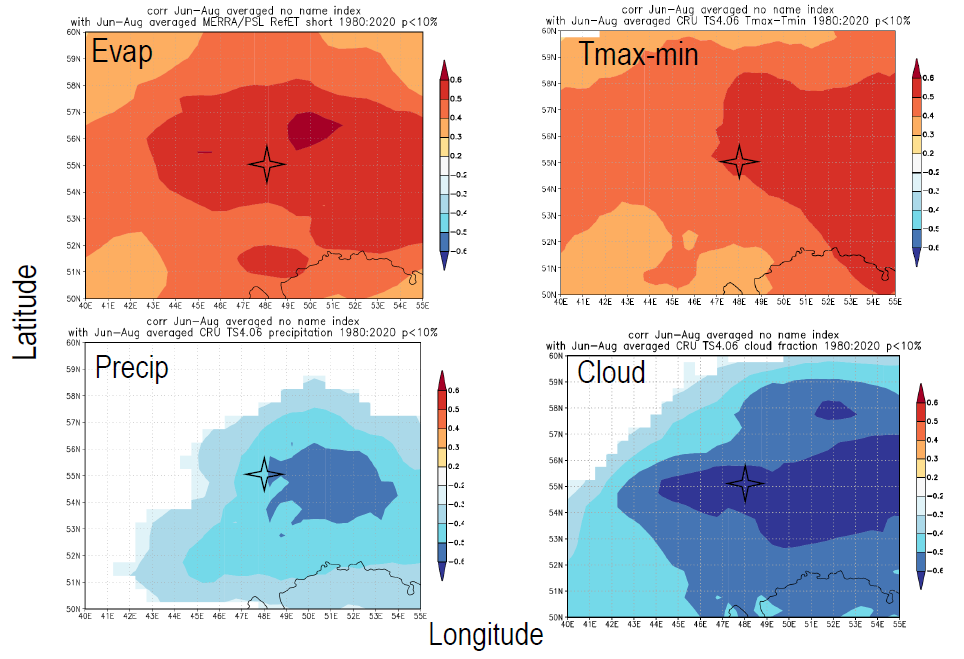
Pearson correlation analysis between detrended tree-ring δ13Cptrw from both study sites showed positive significant (*P < 0.05*) correlations with spring-summer air temperature (April - July) and annual temperature from the local Kazan weather station. The highest correlation was found between annual air temperature and δ13Cpwc for Raifa (r = 0.60) and for UVRT (r = 0.56). Detrended δ13Cpwc showed lower values, but still significant correlations (r = 0.48) for Raifa and for UVRT (r = 0.41).

A negative significant correlation was found between tree-ring δ13C from Raifa and summer (June-August) precipitation (r = - 0.21; *P < 0.05*).

3.4. Spatial correlations patterns

Detrended tree-ring δ13C chronology from UVRT site showed positive significant (*P< 0.05*) spatial correlations within gridded net gridded 0.5x0.5 for the coordinated 50-60°N, and 40-55°E with averaged June-July-August (JJA) evapotranspiration (r = 0.5) (Figure 5a) and JJA Tmax-min (r = 0.5) (Figure 5b), while negative with JJA precipitation (r = -0.5) (Figure 5c) and JJA cloud fraction (r = -0.6) (Figure 5d).

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| (**a**) | (**b**) | |
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| **c)** | (**d**) | |

1. **(b)**

**(c) (d)**

**Figure 5.** Spatial distribution of correlation coefficients within 50-60°N, and 40-55°E gridded 0.5x0.5 net between detrended tree-ring δ13Cptrw from UVRTand averaged June-July-August (JJA) reference evapotranspiration (**a**), differences between maximal and minimal air temperature (Tmax-min) (**b**), precipitation (**c**) and cloud fraction (**d**) computed for the period from 1980-2020. Right vertical scales represent correlation coefficients within the range from − 0.6 (dark blue, negative correlations) to +0.6 (dark red, positive correlations) with the *P < 0.1.*

4. Discussion

The oil and gas industry started to be developed in the Tatarstan Republic, at UVRT site since 1943 [19] and in 1970s reaches the maximum in oil extraction, which was recorded in δ13Cptw the pine forests. Recently the oil and gas production was increased by 3.5 % compared to the past. Further increase of oil and gas production is expected in near future [33]. Accelerating rate of GHG emissions will undouble will change the environment, biodiversity and humans’ health. Only accidents in which a large volume of hydrocarbons released into soil or water are evaluated so far. Therefore, our pioneering study is highlighting how trees could respond to oil and gas development infrastructure near to the deposit and in remote sites location of the region. Therefore, understanding the mechanisms behind of local hydrocarbon emissions from the oil and gas deposits and their contribution to the global GHG emissions is of great importance and should be further investigated among transects and comparing with other available oil and gas deposits infrastructures in the region and outside.

Our results at the tree-ring level shows higher suppression during the oil extraction for the UVRT site, which is also reflected in the tree-ring δ13C values. This can be explained by the negative impact of developed oil and gas infrastructure on the pine forest. Our finding is in line with Pickell et al. [25], who showed anthropogenic disturbance in developed oil and gas activities on forest landscapes in the USA.

Interestingly, pine trees from the natural reserve Raifa site, which is undisturbed by direct human impact show more positive tree-ring with variability compared to the human-induced UVRT site. However, tree-ring δ13C, CH4 and CO2 in soil showed more negative values compared to the oil and gas deposits UVRT site. One of the explanations can be that pine trees from natural reserve site are more sensitive to the impact of greenhouse emissions, while pine trees from the human-induced site are already stressed by the local and global impact. Significant impact of local oil extraction and global hydrocarbon emissions was revealed for UVRT site, which supports our hypothesis that both local and global hydrocarbon emissions affect local pine forests. Increasing of intrinsic water use efficiency (iWUE) along with decreasing tree-ring width chronology from the oil and gas deposits indicate on developing of drought conditions (Figure 4) during the vegetation period, which is confirmed by the local and spatial climatic correlation analyses. Despite site-specific and species-specific differences study by Guerrieri et al. [17] showed that NOx pollutions alter the iWUE by confirming impact of anthropogenic factors on oak trees.

Increasing evapotranspiration and extreme changes in air temperatures, less clouds and decreasing of precipitation lead to developing drier environmental conditions. Pine trees from Raifa site recorded more pronounced drought conditions during July over the period from 1970 to 2021. Further local oil and gas developments and their impacts on forest ecosystems should be better tracked and analysed along the transect for long-term monitoring.

5. Conclusions

We conclude that pine trees from UVRT site indicate on developing unfavorable drier conditions and suppressed tree growth caused by both human-induced oil and deposit infrastructure and natural eco-physiological processes compared to the undisturbed natural reserve Raifa site.,

Understanding the mechanisms behind of local hydrocarbon emissions from the oil and gas deposits and their contribution to the global GHG emissions is of great importance and should be further investigated among transects and comparing with other available oil and gas deposits infrastructures in the region and outside.

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