

GASES AND GAS HYDRATES IN THE EARTH'S CRYOSPHERE

CARBON DIOXIDE RELEASE FROM MELTED GROUND ICE SAMPLES
UNDER CONDITIONS OF AN INCUBATION EXPERIMENTP.B. Semenov^{1,*}, A.O. Kil¹, E.V. Shatrova^{1,2}, N.G. Belova^{3,4}, O.V. Levochkina⁴, M.O. Leibman⁴,
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This work aims to study the quantitative transformation of dissolved organic matter into CO₂ in ground ice samples collected from typical exposures of the Russian Arctic under conditions of an incubation experiment. The CO₂ emission during incubation has two peaks, the first being associated with the utilization of organic carbon dissolved in ground ice; and the second, with the mobilization of organic matter from the solid fraction of melted ground ice. Melted ice samples are characterized by high values of biodegradable dissolved organic carbon (>65%) and a significant positive correlation ($R^2 = 0.82$) between the values of cumulative CO₂ emission and biodegradable dissolved organic carbon. Our data indicate a high potential of ground ice as a source of labile carbon in the ecosystem under thermodenudation.

Keywords: ground ice, dissolved organic matter, carbon dioxide, incubation experiments, biodegradable dissolved organic carbon.

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INTRODUCTION

The state of permafrost in a changing climate is of great scientific and practical interest. According to some researchers, the amount of carbon stored in the permafrost may exceed its content in the modern atmosphere by two times or more [Schuur *et al.*, 2008]. The observed and predicted global warming contributes to the permafrost thawing and, as a consequence, to the release of carbon from buried organic matter (OM) into the modern carbon cycle [McCalley *et al.*, 2014; Dean *et al.*, 2018]. The involvement of relict OM during the degradation of permafrost into the modern carbon cycling leads to the emission of additional amounts of carbon-containing gases – methane (CH₄) and carbon dioxide (CO₂), which can be a trigger for the so-called positive feedback contributing to the acceleration of climate warming [Schuur *et al.*, 2015; Heinz, Zak, 2018; McGuire *et al.*, 2018; Natali *et al.*, 2019].

Massive ground ice, including wedge ice and ice beds, are important components of the permafrost areas in the Russian Arctic in terms of the carbon cycle.

Ice beds and host sediments in the Yamal Peninsula are marked by relatively high methane concentrations that correlate with the organic carbon content in the sediments [Streletskaia *et al.*, 2018; Semenov *et al.*, 2020, 2024; Zadorozhnaya *et al.*, 2022]. Massive ground ice serves as a source of labile dissolved organic matter (DOM) in modern permafrost ecosystems. Surface watercourses formed as a result of ground ice melting transport DOM across landscapes to the base level of erosion. This is accompanied by biogenic mineralization of DOM to CO₂ under aerobic conditions and to CH₄ under anaerobic conditions [Vonk *et al.*, 2013]. All of the above argues for close attention to ground ice as a source of organic matter and greenhouse gases (GHG).

To study GHG emissions, methodological approaches are used that involve in situ gas flux measurements [Kraev *et al.*, 2017; Oblogov *et al.*, 2020; Zadorozhnaya *et al.*, 2022] or experimental incubation with periodic measurements [Vonk *et al.*, 2013; Knoblauch *et al.*, 2018; Shirokova *et al.*, 2019; Prijac *et al.*

al., 2022]. The advantage of the latter is the possibility to monitor carbon transformation in controlled/closed conditions of an incubated vessel. Some studies focus on measuring the loss of organic carbon due to its biogenic mineralization during the incubation and on determining biodegradable dissolved organic carbon (BDOC) [Vonk et al., 2013, 2015; Shirokova et al., 2019]. Other studies are focused on the dynamics of GHG emissions and fluxes over time [Brouchkov, Fukuda, 2002; Tanski et al., 2019; Alekseeva et al., 2021]. It is also necessary to distinguish between methodological approaches that involve measuring the dynamics of DOM and DOC in the filtrates of thawed permafrost samples [Vonk et al., 2013, 2015; Shirokova et al., 2019; Prijac et al., 2022], and approaches that involve the analysis of the dynamics of total and particulate organic matter (POM) and the corresponding carbon fractions: total organic carbon (C_{org} , TOC) and particulate organic carbon (POC) [Knoblauch et al., 2013, 2018; Shakil et al., 2022]. Experiments show that significant and stable generation of CH_4 by methanogenic archaea in anaerobically incubated thawed permafrost samples begins after 3–4 years of zero activity (lag phase), which is probably due to the adaptation of microbiota. Therefore, for experiments to determine methane production in permafrost samples to be reliable, they must be long-term [Knoblauch et al., 2013, 2018]. The fastest and most intense process of biogeochemical OM mobilization is aerobic respiration of bacteria, accompanied by CO_2 emission, which can be demonstrated by short-term incubation experiments [Vonk et al., 2013, 2015; Tanski et al., 2019; Alekseeva et al., 2021]. DOM undoubtedly includes the most labile fraction of OM, primarily spent on biogenic generation of CO_2 , but the POM pool is much larger in terms of total C_{org} content [Shakil et al., 2020]. In this paper, we analyze the dynamics of CO_2 production in filtered and intact samples (initially undisturbed monoliths of ground ice after melting), including three ice bed samples from the Yamal Peninsula thermocirque exposures and two wedge ice samples (from the Yamal Peninsula and from the vicinity of Norilsk city).

The aim of the work is to study, in the course of experimental incubation, some patterns of DOM transformation into GHG in ground ice samples during their melting. The main objectives are to (1) analyze the temporal dynamics of CO_2 emission in ground ice melt samples, (2) quantitatively assess the contribution of solid/suspended matter to CO_2 emission, (3) determine the amount of BDOC and the effect of suspended/solid matter on DOC mineralization under experimental conditions. The idea of this work is not to simulate natural conditions of seasonal melting of ground ice but to demonstrate the potential of ground ice to release labile carbon and generate GHG. In this regard, conditions are created for ex-

perimental incubation that favor biogenic generation of GHG in the aerobic regime in all samples.

STUDY AREA AND GENERAL CHARACTERISTICS OF THE SAMPLES

Five samples of ground ice monoliths were collected in typical exposures of Central Yamal (at the Vaskiny Dachi (VD) Research station) and the environs of Norilsk (N) city (Industrial District, the Daldykan Stream) (Fig. 1). The general description and initial basic geochemical characteristics of the samples are given in Table 1. Figure 2 shows the studied geocryological sections indicating the sampling location of each monolith used in the incubation experiments.

The monolith of massive ice bed (VD1ib) was sampled from the scarp of the thermocirque TC-2A (“Vaskiny Dachi” Research Station), approximately 1.9 m below the upper edge of the exposure represented by alternating layers of “black” ice and “white” transparent (glassy) ice with inclusions of sand and dark gray sandy loam. Gas bubbles in the ice monolith were round in shape and up to 2 mm in diameter. The upper edge of the thermocirque had the absolute height of 21 m a.s.l. with its base at 13.7 m a.s.l. (Figs. 1b, 2a, and 2b).

Monolith VD2ib was sampled from the scarp of thermocirque TC-5 (“Vaskiny Dachi” Research Station) from the ice exposure approximately 3 m below the upper edge, at the interface of gray loam and transparent glassy ice. This thermocirque was located on a slope and has its upper edge at 25 m a.s.l. and its base at 3 m a.s.l. (Figs. 1b, 2a, and 2b).

Monolith VD3ib was sampled from an ice layer exposed in the eastern scarp of the TC-5 thermocirque. The ice lens was located 120 cm below the upper edge of the thermocirque and had a thickness of about 40 cm and visible width about 1.5 m. The ice was clean, transparent, with numerous bubbles (Figs. 1b, 2a, and 2b).

Ice wedge sample VDiw was taken in a pit dug in a polygonal peat bog (“Vaskiny Dachi” Research Station). The head of the Holocene ice wedge was exposed at a depth of about 0.5 m in an interpolygonal trough. The ice was almost transparent with characteristic vertical stratification. The monolith was collected to the right of the ice wedge axis (Figs. 1b, 2a, and 2b).

Ice wedge sample Niw was taken a Holocene peat bog on the right bank of the Daldykan Stream (Norilsk Industrial Region), 200 m from the channel. The peat bog extended from north to south for 150 m and had a width of about 50 m. The polygonal relief was at the degradation stage, and the difference in height between the centers of polygons and interpolygonal troughs could be up to 2 m. The diameter of the polygons varied within 8–13 m (up to 17 m) (Figs. 1c, 2a, and 2b).

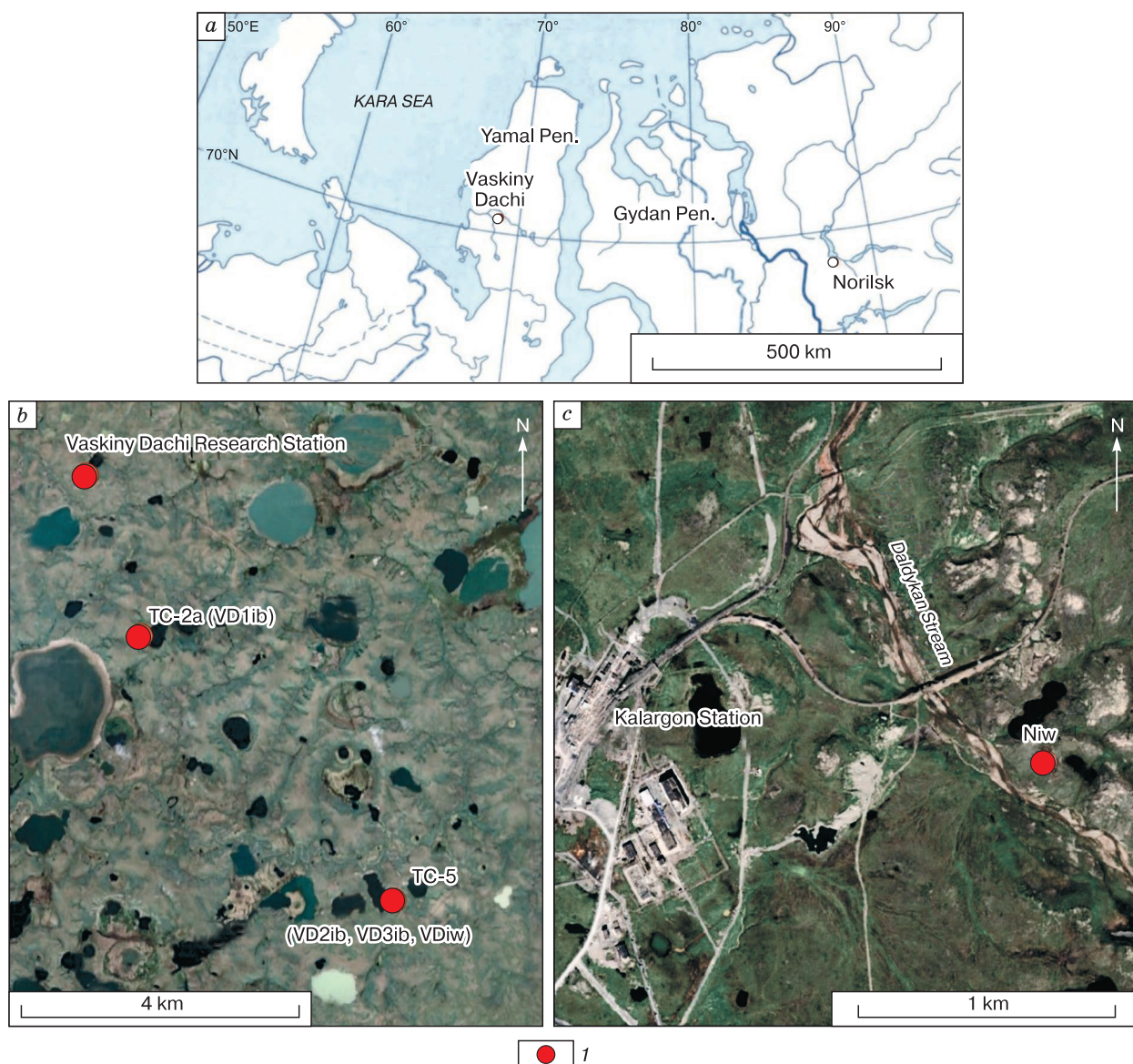


Fig. 1. An overview map of the ground ice sampling (a); a detailed map of sampling location (VD1ib, VD2ib, VD3ib, VDiw) in Central Yamal (b); a detailed map of sampling location (Niw) in Norilsk Industrial Region, the Daldykan Stream (c).

1 – sampling sites; TC – thermocircue, ib – ice beds, iw – ice wedges, VD – Vaskiny Dachi, N – Norilsk.

Table 1. General characteristics and initial geochemical parameters of ice samples

Sample ID	Ice type	Sampling site	Lithogenic fraction, wt. %	TDS, mg/L	pH	DOC, mg/L	CH ₄ , ppmV	CO ₂ , ppmV
VD1ib	Ice bed	Yamal Peninsula, "Vaskiny Dachi" Research Station	11.33	74.58	7.82	42.66	14 802.73	2435.95
VD2ib	Ice bed		41.89	397.01	7.08	126.53	3485.78	2030.94
VD3ib	Ice bed		3.61	40.57	7.20	7.14	1019.20	2138.37
VDiw	Ice wedge		2.95	20.90	6.19	62.34	418.15	34 998.70
Niw	Ice wedge	Norilsk, Daldykan Stream	0.01	9.27	6.62	5.35	3.90	1334.59

Note: TDS – Total Dissolved Solids in water; pH – hydrogen index, DOC – dissolved organic carbon, CH₄ – methane, CO₂ – carbon dioxide, ppmV – parts per million by volume; Sample ID: ib – ice bed; iw – ice wedge, VD – Vaskiny Dachi, N – Norilsk.



Fig. 2. Cryolithological sections with monolith sampling locations (a); ground ice monoliths used for incubation experiments (b); vials with ground ice melts (c).

1 – sampling points; filtered variants of melts are marked with “f”; ib – ice beds, iw – ice wedges, VD – Vaskiny Dachy, N – Norilsk.

MATERIALS AND METHODS

To study the initial gas composition of the samples, ground ice monoliths were placed in 75-mL glass vials. Vials were pre-washed with 1 N HCl and deionized water, then dried and weighed. Each sample placed in the vial was weighed to obtain the sample mass. The space above the sample (headspace) was washed with pure argon and hermetically sealed. The sealed vials were shaken using an orbital shaker (Heidolph Unimax 2010) for 3 h at maximum rotation speed (3500 rpm). The content of solid material (lithogenic fraction in % of the initial sample mass), gas composition (CH_4 , CO_2 , N_2), and DOC in ice

melts were measured according to the methods described in previous publications [Semenov *et al.*, 2020, 2024; Pismeniuk *et al.*, 2023].

For the experimental studies, ice monoliths were melted at $+4^\circ\text{C}$ for 24–48 hours. The resulting initial melts of each of the five samples were used to prepare two experimental variants (subsamples): intact (unfiltered) and filtered ($0.45\ \mu\text{m}$). Comparison of the intact and filtered variants allowed for the selective determination of CO_2 and biodegradable DOC associated with the dissolved and suspended (lithogenic) fractions of the ground ice samples, respectively. The filtered samples were marked as “f” (fVD1ib, etc.). Due to the limited amount of material (ground ice

monoliths), only three out of five samples were duplicated (VD2ib, VD3ib, Niw). Overall, 16 samples were subjected to the incubation. Figure 2c shows photographs of incubation variants of ground ice melts.

Suspensions (intact melts) and melt filtrates of ground ice samples were poured into pre-weighed and washed with 1 N HCl and deionized water vials; approximately 100 mL of material was placed in each vial according to the scale marked on the vial. The vials with samples were weighed and the mass of the samples was recorded and subsequently used for quantitative calculations. The main study was based on the experimental incubation of samples under aerobic conditions at room temperature, tracking the dynamics of CO₂, and the amount of BDOC at the beginning and at the end of the incubation in each variant [Vonk *et al.*, 2013, 2015; Shirokova *et al.*, 2019; Tanski *et al.*, 2019; Alekseeva *et al.*, 2021]. To equalize the conditions of “microbiological colonization” of the incubated 16 samples the inoculation was used. Filtrate of an aqueous suspension of cultural soil (0.75 µm, Watman GF-F) was used as an inoculum injected into each sample (100 µL). This method allows introducing a sufficient amount of active aerobic microbiota into each incubated sample [Vonk *et al.*, 2013].

The duration of the incubation experiment was 61 days. During the incubation, periodic sampling was performed (in addition to the initial point) on days 6, 15, 20, 26, 38, 50, and 61. The concentration of CO₂ and other gases was measured after shaking the incubation flasks for 3 hours on an orbital shaker (Heidolph Unimax 2010). The procedure for collecting gas and filtrate samples, as well as measuring gas concentrations (CO₂, etc.) and DOC, are similar to those described above for determining the initial geochemical characteristics of ground ice samples. For each measurement, the current mass of the sample and the volume of gas (headspace) were taken into account. Gas concentrations were calculated using the ideal gas equation, Henry's Law, and Bunsen coefficients [Yamamoto *et al.*, 1976; Ioffe, Vitenberg, 1984]. The CO₂ generation (emission) during the experiment was expressed as the mass of carbon CO₂ per mass of melt (CO₂-C, µg/g), as well as the mass of carbon per mass of melt per day of the experiment (CO₂-C, (µg/g)/day) [Knoblauch *et al.*, 2013]. Changes in the CO₂ concentration over time were plotted as two curves: a dynamic curve, where the amount of CO₂ released during each interval of the incubation was visualized, and a cumulative curve, where the portions of CO₂ released during each interval were summed up. Thus, the end point of the cumulative curve characterized the maximum amount of CO₂ released during the experiment. The BDOC content was determined by the difference in its concentrations at the beginning and end of the incubation test [Vonk *et al.*, 2013].

RESULTS

Initial geochemical characteristics of the samples

The work involved three samples of ice beds (ib) and two samples of ice wedges (iw). Sample VD2ib had the highest content of lithogenic fraction reaching 41.89 wt.% (Table 1). The lowest content of lithogenic fraction was in the ice wedge sample Niw collected in the vicinity of Norilsk. Both ice wedge samples (VDiw and Niw) had pH values <7 (up to 6.19), which was probably due to their localization within the polygonal peatlands. The highest pH value (7.82) was recorded in sample VD1ib. The maximum value of total mineralization (TDS) was found in sample VD2ib 397.01 mg/L, while the minimum (9.266 mg/L) was measured in sample Niw. Sample VD2ib was enriched in dissolved salts by more than 5 times compared to ice bed samples VD1ib and VD3ib, which was probably due to a higher content of the lithogenic fraction captured by ice from the enclosing sediments of marine origin.

The maximum DOC content (126.53 mg/L) in sample VD2ib was 23.6 times higher than the minimum DOC content (5.35 mg/L) in sample Niw. The sample from the Holocene ice wedge VDiw was remarkable for the high DOC content (62.34 mg/L), and an abnormally high CO₂ concentration (34 598 ppmV) in the gas phase of the melt. In all samples, CO₂ concentrations were many times higher than the modern atmospheric background values, indicating the enrichment of the source water in carbon dioxide. More or less similar values of CO₂ concentration were determined in ice bed samples: 2435.95 ppmV (VD1ib), 2030.94 (VD2ib), and 2138.37 ppmV (VD3ib). The maximum concentration of methane (CH₄) measured in the VD1ib sample – 14 802.72 ppmV – was many times higher than all the other values measured in this experiment. The minimum concentration of CH₄ (3.90 ppmV), close to the equilibrium atmospheric concentration, was characteristic of the Niw sample. In general, ice wedge samples were characterized by lower methane concentrations than ice bed samples, but the range of variation between them exceeded the difference between the lowest concentration of CH₄ in ice beds (1019.20 ppmV, sample VD3ib) and the highest concentration of methane in ice wedges (418.14 ppmV, sample VDiw). The studied collection of the ground ice samples is sufficiently diverse in the distribution of key parameters to represent material for experimental studies.

Greenhouse Gas Generation under Experimental Incubation

The results of gas composition measurements during experimental aerobic incubation of ground ice melts demonstrate that CO₂ generation obviously differs in various ground ice samples, as well as in in-

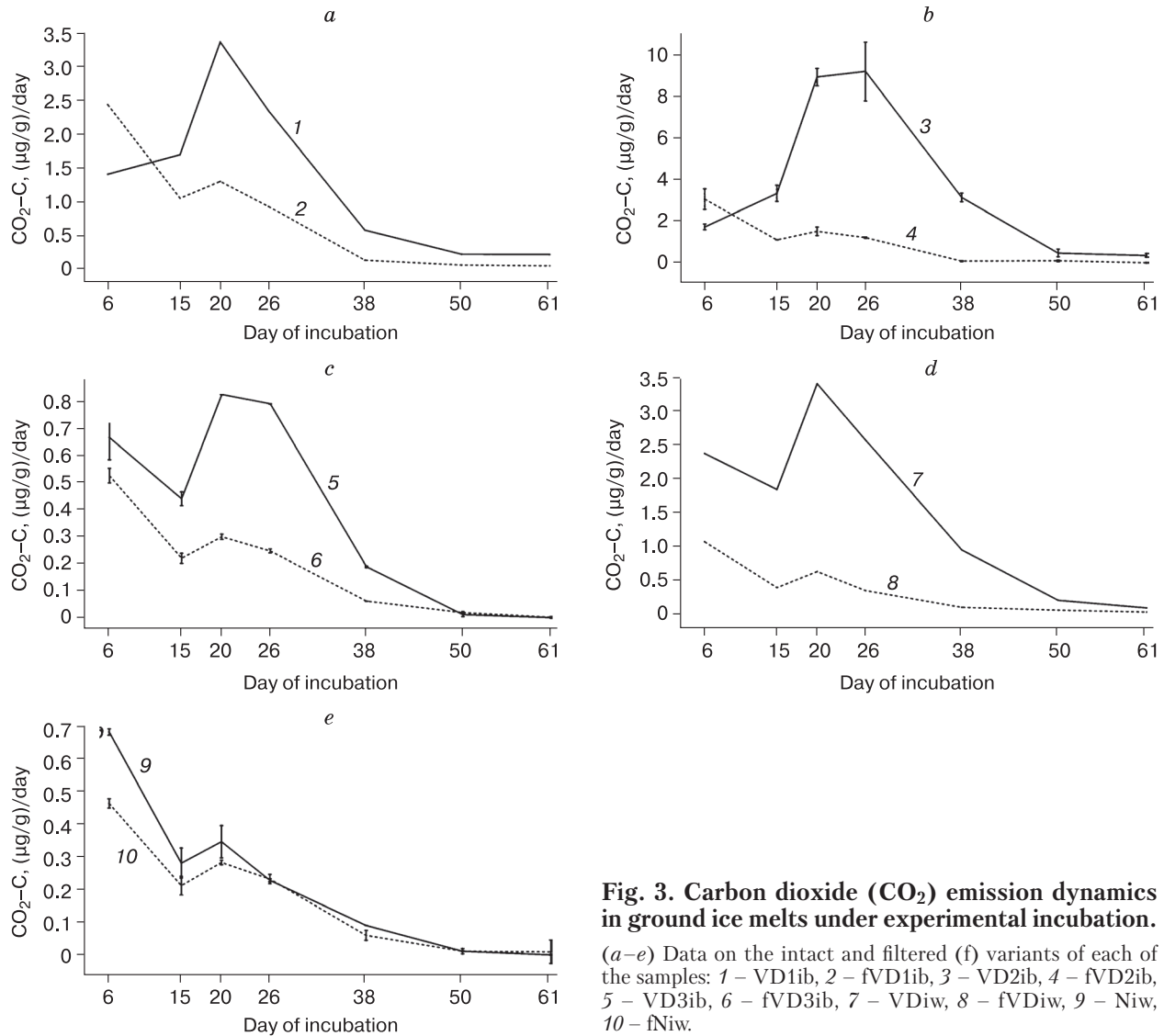


Fig. 3. Carbon dioxide (CO₂) emission dynamics in ground ice melts under experimental incubation.

(a–e) Data on the intact and filtered (f) variants of each of the samples: 1 – VD1ib, 2 – fVD1ib, 3 – VD2ib, 4 – fVD2ib, 5 – VD3ib, 6 – fVD3ib, 7 – VDiw, 8 – fVDiw, 9 – Niw, 10 – fNiw.

tact and filtered variants of each of the studied samples. No reliable increase in methane concentration in the gas phase was recorded in any of the samples during the experimental incubation of ground ice melts. In this regard, no data on methane emission are provided in the text or in the illustrations.

Diagrams illustrating CO₂ emission in ground ice samples are shown in Figs. 3 and 4. The plots indicate the dynamics of CO₂ emission for each of the two variants (intact and filtered). The maximum value of cumulative CO₂ emission (Figs. 4c and 4d) for the entire incubation period (61 days) was 173.40 CO₂-C, μg/g in the intact ice bed sample VD2ib from the central part of Yamal, which had the highest content of the solid fraction among the analyzed ice samples (41.8 wt.%). The minimum value of cumulative CO₂ emission (10.63 CO₂-C, μg/g) was found in the fil-

tered melt of sample Niw prepared from a transparent ice wedge with an extremely low content of the lithogenic fraction (~0.01 wt.%). Thus, the measured minimum and maximum values of CO₂ cumulative emission differ by more than 17 times. The curves of the CO₂ generation dynamics in intact samples are characterized by a sharp rise during 15–26 days of incubation, when the maximum values of the average daily CO₂ emission are observed (up to 9.160 CO₂-C, μg/(g·day) in the VD2ib sample). The standard deviation (SD) values between the duplicate samples of CO₂ emission measurements, plotted on the graphs as error bars for the VD2ib, VD3ib and Niw samples (Figs. 3b, 3c, 3e; Figs. 4a–4d), are notably higher in the intact variants than in the filtered ones, which is especially noticeable for VD2ib sample with the highest content of the lithogenic fraction.

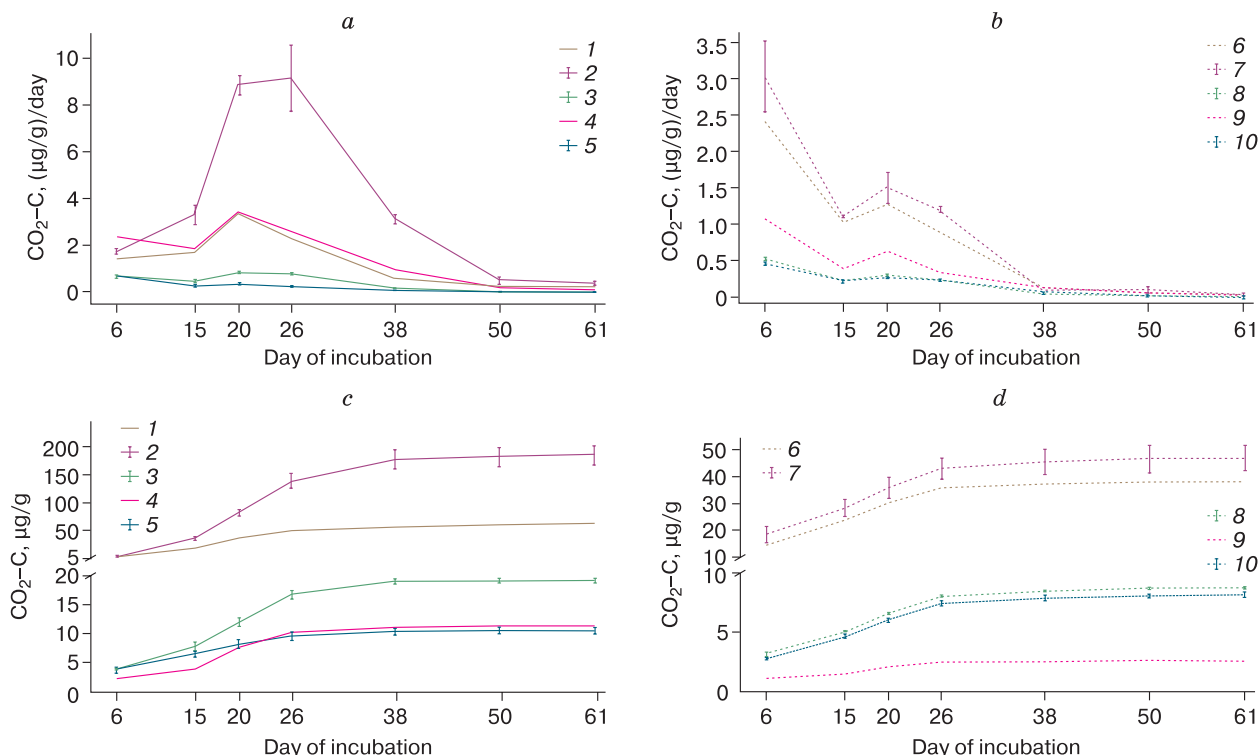


Fig. 4. Carbon dioxide (CO₂) emission from the ground ice melts under experimental incubation.

(a, b) – emission dynamics curves; (c, d) – cumulative emission curves. 1–5: intact (continuous lines, 1 – VD1ib, 2 – VD2ib, 3 – VD3ib, 4 – VDiW, 5 – Niw), 6–10: filtered (dotted lines, 6 – fVD1ib, 7 – fVD2ib, 8 – fVD3ib, 9 – fVDiW, 10 – fNiw).

Biodegradable dissolved organic carbon (BDOC) under experimental incubation conditions

BDOC values (calculated as a difference in DOC concentrations at the initial and final points of incubation) vary from 83.39 mg/L (ice bed sample VD2ib with the highest solid fraction content and cumulative CO₂ emission value for the entire incubation period) to 0.27 mg/L in the filtrate of transparent melt (Niw) with the lowest values of the above parameters. The DOC data under experimental conditions are summarized in Table 2. In general, for the studied samples, BDOC demonstrates higher values in the intact variants. The ratios of BDOC concentrations in intact and filtered samples are (in descending order): 13.2 (VD2ib), 2.23 (VD1ib), 1.814 (Niw), 1.55 (VD3ib). Sample VDiW is an exception: it demonstrates a higher BDOC value in the filtered variant (2.98 mg/L versus 1.30 mg/L in the intact sample).

DISCUSSION

The work involves a collection of five samples, four of which were obtained in the area of “Vaskiny Dachi” Research Station. Ground ice exposures and permafrost thawing conditions in this location have been a subject of numerous studies [Dvornikov *et al.*,

2017; Khomutov *et al.*, 2017; Leibman, Khomutov, 2019; Savvichev *et al.*, 2021].

The curves of the CO₂ emission dynamics in the incubated samples generally form different patterns for the intact and filtered variants. The former are characterized by peak values of the average daily CO₂ emission in the period from the 15th to the 38th day of incubation with a maximum in the range of 26th–28th day. The latter are characterized by the highest intensity in the period from the 6th to the 15th day with a maximum at the earliest stage of incubation (the 6th day). The temporal dynamics of CO₂ generation undoubtedly reflects the mobilization of labile OM into the local carbon cycle. Probably, the first stage of peak CO₂ emission is associated with the use of the most labile fraction of ground ice DOC, which already resides in the solution and is directly accessible to microorganisms. Intensive CO₂ generation during the first days of incubation was previously noted for various frozen rocks enriched in labile OM [Lee *et al.*, 2012; Knoblauch *et al.*, 2013]. The next peak of CO₂ emission (15th–38th day), most pronounced in intact samples, is apparently due to the supply of an additional portion of organic carbon from the solid component of ice melts. This portion plays a significant quantitative role in the resulting (cumulative) CO₂

Table 2. Concentrations of dissolved organic carbon (DOC) and biodegradable dissolved organic carbon (BDOC) in an incubation experiment

Sample	DOC _{init}	DOC _{fin}	BDOC	
	mg/L		mg/L	%
VD1ib	42.66	25.28	17.38	40.74
fVD1ib		34.88	7.78	18.24
VD2ib (1)	126.53	43.14	83.39	65.91
VD2ib (2)		48.22	78.32	61.90
VD2ib av			80.85	63.90
VD2ib, SD			3.59	2.84
fVD2ib (1)	126.53	119.47	7.06	5.58
fVD2ib (2)		121.35	5.19	4.10
fVD2ib av			6.12	4.84
fVD2ib, SD			1.33	1.05
VD3ib (1)	7.14	4.74	2.40	33.61
VD3ib (2)		4.88	2.26	31.65
VD3ib av			2.33	32.63
VD3ib, SD			0.10	1.39
fVD3ib (1)	7.14	5.51	1.63	22.83
fVD3ib (2)		5.78	1.36	19.05
fVD3ib av			1.50	20.94
fVD3ib, SD			0.19	2.67
VDiw	62.34	61.04	1.30	2.09
fVDiw		59.36	2.98	4.78
Niw (1)	5.35	4.75	0.60	11.21
Niw (2)		4.97	0.38	7.10
Niw av			0.49	9.16
VDiw, SD			0.16	2.91
fNiw (1)	5.35	5.04	0.31	5.79
fNiw (2)		5.12	0.23	4.30
fNiw av			0.27	5.05
fNiw, SD			0.06	1.06

Note: DOC – dissolved organic carbon, BDOC – biodegradable dissolved organic carbon, DOC_{init} and DOC_{fin} – DOC values before and after incubation, respectively; av – average value; SD – standard deviation; f – filtered variants; ib – ice beds; iw – ice wedges, VD – Vaskiny Dachy, N – Norilsk.

emission from ice melts. The curves of CO₂ dynamics emission in the intact and filtered variants of the Niw sample, which contains almost no solid inclusions, practically coincide, illustrating the minor role of suspended matter in the mineralization of OM to CO₂ in this sample. The mobilization of OM from the solid phase can be associated with desorption from the organomineral matrix and with the dissolution/destruction of detrital forms of OM in the sample [Groeneveld *et al.*, 2020]. Suspended material of the incubated mixture also contributes to the fixation and development of microbial biomass [Battin *et al.*, 2008; Shakil *et al.*, 2020]. The above-mentioned processes are certainly activated by ice melting and high temperatures in the incubated melts (+22°C) during the incubation period. It should be noted that in this

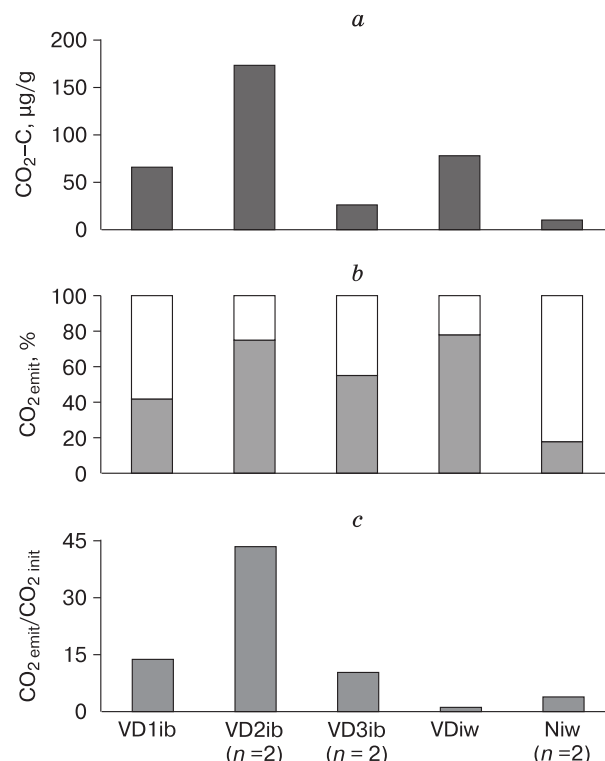


Fig. 5. Comparison of cumulative CO₂ emission values in the ground ice melt as a result of 61-day incubation (a); contribution of dissolved and suspended OM (associated with the solid phase of melts) to CO₂ emission (b), the ratio of cumulative CO₂ emission to the initial CO₂ concentration in the ground ice sample (c).

For duplicate incubations ($n = 2$) averaged values (VD2ib, VD3ib, Niw) are shown.

work, the authors did not aim to reproduce the natural conditions of ground ice melting, but focused on comparing data on different samples placed in equal conditions of a short-term incubation experiment.

It follows from Fig. 5a that the highest values of cumulative emission are characteristic of two ground ice samples, particularly the ice bed sample VD2ib (173.40 CO₂-C, μg/g) and the ice wedge sample VDiw (78.035 CO₂-C, μg/g), which generally illustrates quite comparable potential for CO₂ generation out of ground ice of different origin. It is curious that the above-mentioned samples (VD2ib and VDiw), collected from the thermocirques of central Yamal, are characterized by similar values of the suspended organic matter contribution (75.02 and 77.95%, respectively) to the cumulative CO₂ emission with a more than 20-fold difference in the solid fraction content of the incubated melts (41.88 and 2.95% by weight, respectively). This indicates the critical importance of the solid fraction of ground ice as a source of biolabile DOM mineralized by aerobic microbiota

with the release of CO₂, and also confirms the special role of ice wedges in the local carbon cycle during ground ice melting in thermocirques. Similar patterns were noted in a number of studies describing the process of OM mobilization from suspended material of frozen rocks of thermokarst landscapes [Tanski et al., 2017; Shakil et al., 2020]. In addition, the literature describes the stimulating effect of ice wedge melts on the mineralization of DOM in aqueous extracts of the ice complex under experimental incubation conditions (the Kolyma River bank, Duvanny Yar) due to the co-metabolism known as the priming effect [Vonk et al., 2013; Textor et al., 2019]. A comparison of the initial CO₂ concentrations in the ice bed melts and the concentrations of CO₂ released as a result of the labile OM biogenic mineralization (CO₂ emissions during incubation) shows that these parameters are apparently not related. This is illustrated by the plot in Fig. 5c, where the above-mentioned variables ratio (CO₂ emission/CO₂ initial) shows a significant scattering that does not follow any pattern. Thus, the initial CO₂ concentration in the ice bed sample does not predict the potential for CO₂ generation from the enclosed OM.

Based on the temporal dynamics of the ground ice OM biogenic mineralization during the incubation, we suggest the following phases of CO₂ emission: the first phase (6th to 15th day of incubation) is associated with mobilization of DOM in the melt; the second one, with the release of DOM from the suspended matter (15th to 38th day); then, a decrease in the CO₂ emission is observed in all incubated samples (38th to 61st day). A sharp fall in the activity of aerobic respiration (the main biochemical process providing mineralization of OM to CO₂) on the 28th to 40th day of incubation may be associated with the depletion of labile OM or bioavailable forms of nitrogen, limiting the intensity of biochemical processes in the obvious absence of oxygen starvation (the O₂ concentration in the head space of the samples did not fall below 16%). Probably, a similar pattern of CO₂ emission with two peaks caused by the sequential utilization of DOM and POM, respectively, is also a characteristic of natural conditions of thermodenudation within ground ice exposures.

A correct comparison of the data on cumulative CO₂ emission from ground ice samples with similar data available in the literature on frozen rocks is not entirely feasible, since in the latter cases the values are recalculated per dry sample weight [Knoblauch et al., 2013; Tanski et al., 2019]. In the present work, the amount of CO₂ released during incubation is recalculated per mass of melted ground ice samples containing both water and solid fraction. However, even very rough comparisons taking into account the above-mentioned discrepancies indicate significantly lower CO₂ emission by ground ice melts in relation to bot-

tom sediments or frozen rock samples [Knoblauch et al., 2013; Tanski et al., 2019; Alekseeva et al., 2021].

Incubation experiments demonstrate a significant loss of labile (biodegradable) DOC (BDOC) during ice melt incubation. The maximum BDOC recorded is 65.91% over 61 days of incubation in the sample VD2ib, which is also notable for the maximum initial DOC concentration (126.53 mg/L) and maximum solid fraction content of 41.88% by weight. Sample VD2ib is also characterized by an extremely high total dissolved solids (TDS) value of 397.01 mg/L, which may indirectly indicate the contribution of marine OM to the labile carbon pool that provides the maximum CO₂ emission during the experiment. The mentioned BDOC value in the VD2ib sample (65.91% over 61 days) is comparable with the values (about 34% over 14 days of incubation) reported for surface water samples in the Pleistocene ice complex zone sampled on the Kolyma River bank [Vonk et al., 2013, 2015]. Special attention should be paid to the higher BDOC values in the intact variants compared to the filtered ones, which are typical for all samples except for VDiw (Fig. 6). Thus, the ratios of the BDOC values in the intact variants to the filtered ones are in descending order: 13.2 (VD2ib), 2.23 (VD1ib), 1.81 (NiW), 1.56 (VD3ib). This feature contradicts our initial expectations, according to which a more intensive DOC consumption should be observed in filtered variants, where DOC is the only source of energy for aerobic chemoorganotrophic microbiota, whereas in intact melts there is an additional source of OM associated with the solid phase (SOM). Based on this data, we cannot exclude that more intensive DOC consumption and higher values of CO₂ emission in the intact samples are caused by the activation of biogeochemical processes

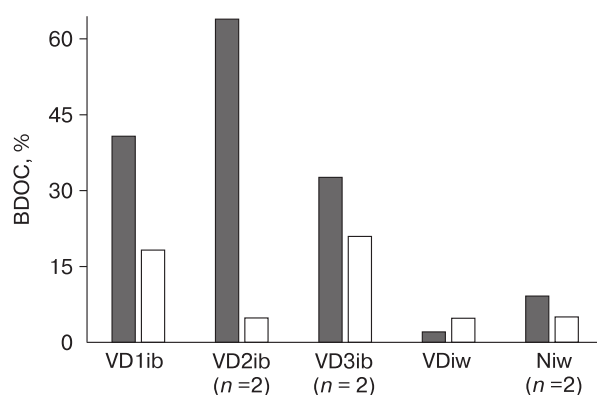


Fig. 6. Comparison of biodegradable dissolved organic carbon (BDOC) concentrations in the ground ice melt as a result of 61-day incubation.

Dark filled columns – intact variants, white filled columns – filtered variants. For duplicate incubations ($n = 2$) average values are shown (VD2ib, VD3ib, Niw).

BDOC – biodegradable dissolved organic carbon.

in the presence of solid material rather than by the release of the additional portion of DOC from the SOM pool. However, in this work, involving a rather narrow set of both experimental variants and variables, we prefer a more straightforward hypothesis that the labile DOM is released from the solid phase of melts (due to desorption and dissolution), which is based mainly on the comparison of the cumulative CO₂ emission values in the intact and filtered melts. The sample of ice bed VD2ib is remarkable for the greatest influence of the solid fraction on the mineralization of DOM, and the sample Niw is notable for the opposite trend, where a large value of BDOC is noted for the filtered variant. Further detailed studies should bring us closer to understanding the obtained BDOC distribution patterns.

Figure 7 shows a graph of the relationship between the values of cumulative CO₂ emission and concentrations of BDOC in ground ice melts indicating a significant positive correlation ($R^2 = 0.82$, $p = 0.003$). Both axes of the plot have a logarithmic dimension for a clearer presentation of the low values. A previously mentioned feature is evident here: for the majority of samples there is a more significant decrease of DOM in the intact variants compared to the filtered ones, which is associated with a more intense CO₂ emission. The only exception is the ice wedge sample VDiw collected at the “Vaskiny Dachi” Research Station: its intact variant shows disproportionately high values of CO₂ emission (78.035 CO₂-C, µg/g) in combination with relatively low values of BDOC. Formally, this can be explained by the compensation of the BDOC loss due to extraction from the solid phase. Taking into account the low content of the solid fraction in the VDiw melt (2.95%

by mass), we assume the presence of weakly transformed detrital forms of OM which replenish the labile DOM through dissolving in the aqueous phase of the melt. We should also consider the massive ice bed sample VD3ib with higher ratio of CO₂ emission to the BDOC content than of the rest of the melts, except for VDiw. This fact is difficult to interpret unequivocally at this stage of research, but it definitely characterizes the specifics of the composition of DOM utilized by aerobic chemoorganotrophic microbiota during incubation. Apparently, the correspondence of the BDOC values to cumulative CO₂ emission is a promising tool for the analysis of experimental data, as well as the differentiation of ground ice samples in relation to the local carbon cycle. Further studies with ground ice monoliths at the level of the dissolved and suspended organic matter chemical composition, accompanied by CO₂ and BDOC measurements, will allow us to clarify the patterns obtained in this work and improve the diagnostic approach based on the experimental incubation results.

The results of this study indicate a sufficiently high lability of the ground ice DOM, as well as complex and multifaceted interactions between DOM and SOM, which do not fit into mechanistic concepts.

CONCLUSIONS

The studies have shown that the dynamics of CO₂ generation reflects two temporal stages of labile OM mobilization into the local carbon cycle, where the first stage is associated with the use of exclusively ground ice DOM, and the second is due to the mobilization of labile OM from the solid fraction of ground ice melts. The maximum measured value of cumulative CO₂ emission is 17 times higher than the minimum, indicating high variability of the CO₂ emission potential of melting ground ice.

For ground ice samples relatively enriched in the solid fraction, the significance of suspended organic matter (associated with the solid fraction of melts) has been demonstrated as a source of biochemically labile DOM readily mineralized by aerobic microbiota with the release of CO₂. At the same time, the relative contribution of solid material is different, which indicates the influence of its composition on the CO₂ emission potential. Incubation experiments show a drastic decrease in biodegradable DOM, up to 65.91% in 61 days indicating high lability of the ground ice organic matter. A significant positive correlation ($R^2 = 0.82$) was found between the values of cumulative CO₂ emission and the values of BDOC in ground ice melts. At the same time, higher values of BDOC in intact variants compared to filtered ones (where DOM serves as the only carbon source for the generated CO₂) are characteristic of most ground ice samples.

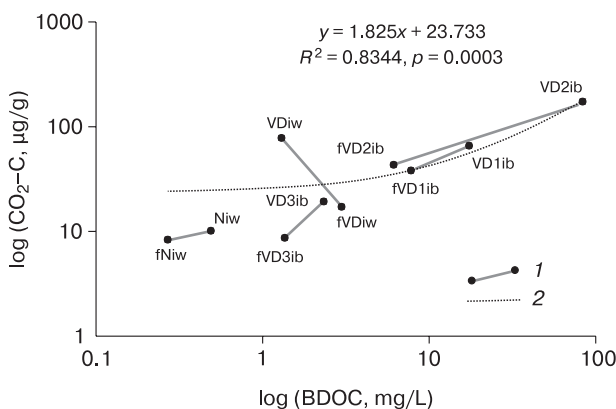


Fig. 7. Correlation between the content of biodegradable dissolved organic carbon (BDOC) and cumulative CO₂ emission measured in the aerobic incubation experiment (61 days).

1 – the lines connecting points for filtered (f) and intact variants of corresponding ground ice samples; 2 – regression trendline. For other designations, see Figs. 1 and 5.

The results of this study indicate a sufficiently high lability of the ground ice DOM, as well as complex and multifaceted interactions between DOM and SOM, which do not fit into mechanistic concepts.

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