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Uric acid in the surface waters of Spitsbergen and its role in the dissolution processes which affect carbonate rocks

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Abstract: Using High Performance Liquid Chromatography, concentrations of uric acid in the surface waters of two non-glaciated catchments (Fugle and Dynamisk) on Spitsbergen were measured. Measurements of specific conductivity enabled us to perform tests on the dissolution of the carbonate rocks present in both catchments in both natural and aqueous solutions of uric acid. Samples of calcium urate were made and its water solubility determined. Given a knowledge of concentrations of uric acid, calcium ions and calcium urate solubility product, an estimate of the role of uric acid in the dissolution of carbonate rocks was possible. Uric acid increases the dissolution of carbonate rocks by c. 12.5% in case of the Fugle catchment and 7% in Dynamisk.

Key words: Spitsbergen, Hornsund, Billefjorden, uric acid, rock carbonate solubility.

Introduction

Owing to the high concentration of pelagic food and a rich benthos along the western sea-coast of Spitsbergen (Węśławski 1993), seabird colonies numbering many thousands of birds are present here (Mehlum and Fjeld 1987). Dovekies (also known as Little Auks – *Alle alle* L.) usually reach Svalbard during the first days of April (about two months before nesting) and depart at the end of August (Stempniewicz 1978; Isaksen and Bakken 1995), whereas the process of thawing in unglaciated catchments starts in the second half of May or in June (Leszkiewicz 1987). Hydrological activity in unglaciated polar catchments usually lasts from May to September (Pulina *et al.* 1984) and the contamination by birds

causes significant variations in the chemical composition of surface waters flowing through the bird colonies (Krzyszowska 1984). Dovekies from the largest colony in Hornsund collectively consume *c.* 700 tons of planktonic food each season (Stempniewicz and Węśławski 1992), which results in the excretion of uric acid; this can amount to as much as 30% of dry faeces (Lindeboom 1984; Mizutani *et al.* 1985). Its presence in water, even at a very limited solubility (20 mg dm⁻³ at 0°C), significantly acidifies the water. This acid ($K = 1.3 \times 10^{-4}$) is significantly stronger than the carbonate acid ($K = 4.3 \times 10^{-7}$) present in waters acidified by the CO₂ present in the atmosphere and local soils.

Many authors *e.g.* Hutchinson (1950), Speir and Cowling (1984), Speir and Ross (1984) have drawn attention to the rapid decomposition of uric acid in the ornithogenic soils of the Antarctic in summer seasons but none of those has discussed the presence and influence of uricase (urate oxidase) – the enzyme responsible for the rapid decomposition of uric acid. Arctic and Antarctic environments differ in respect that no ornithogenic soils have been reported in Svalbard, despite there being large amounts of biogenic matter in the soils (Klekowski and Opaliński 1986).

The objectives of this study were to determine the extend of uric acid in the surface waters of two non-glaciated catchments of Spitsbergen which are remote from each other (200 km) and its role in dissolution of carbonate rocks present below the soil cover and carbonate mineral particles within the soil.

Materials and methods

Location. — Surveys were conducted concurrently on two non-glaciated polar catchments of Spitsbergen during the summers of 2001 and 2002. Fugle catchment is situated along the northern shore of Hornsund (SW Spitsbergen) (Fig. 1), whereas Dynamisk is located in Central Spitsbergen (Fig. 2). Billefjorden makes the climate of Dynamisk catchment significantly different from that of the Fugle catchment, which borders the open Atlantic ocean. When the data concerning the two basic meteorological parameters (mean air temperature and the total amount of precipitation) are compared for the period 6th July to 15th September for both catchments during consecutive years, the climatic differences are obvious (Table 1).

The Fugle Basin (1.36 km²) is located partly on raised marine terraces but mainly on the slopes of coastal mountains (Ariekammen 512 m a.s.l. and Fugleberget 569 m a.s.l.) (Pulina *et al.* 1984). The bedrock consists of metamorphic rocks (phyllites and schists) of the Ariekammen Formation (Isbjørnhamna Group) and carbonate rocks (mainly gray marbles and calcareous schists) (Birkenmajer 1990). The rich tundra plant communities which cover the slopes and terraces of Fugle catchment, are supported by large Dovekies colony on the slope of Ariekam-

Table 1
 Comparison of basic meteorological parameters for the Dynamisk and Fugle catchments in the period of 06.07–15.09 in the years 2001 and 2002.

Period	Dynamisk catchment		Fugle catchment	
	Air temp.*	Precipitation**	Air temp.*	Precipitation**
	[°C]	[mm]	[°C]	[mm]
06.07–15.09.2001	6.7	57.3	4.8	107.8
06.07–15.09.2002	6.8	30.0	4.9	130.7

* average of daily means

** total daily amount

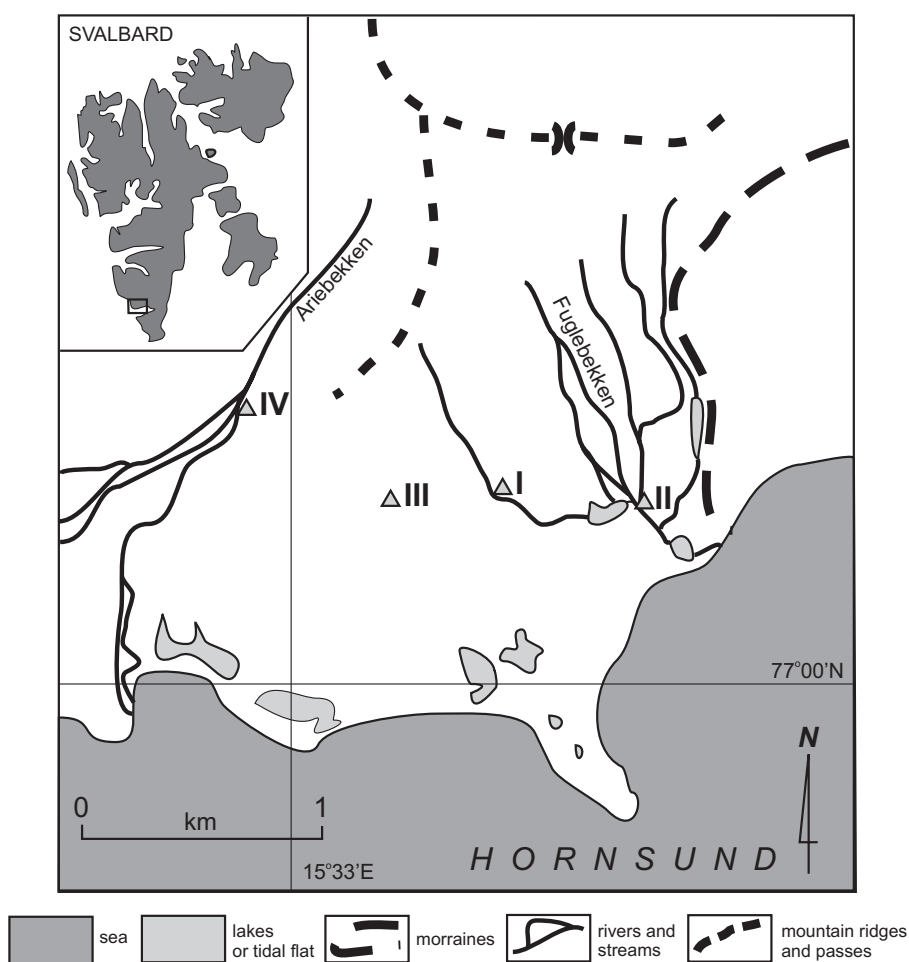


Fig. 1. Water sampling locations (I–IV) on the territory and in the vicinity of the Fugle catchment (SW Spitsbergen).

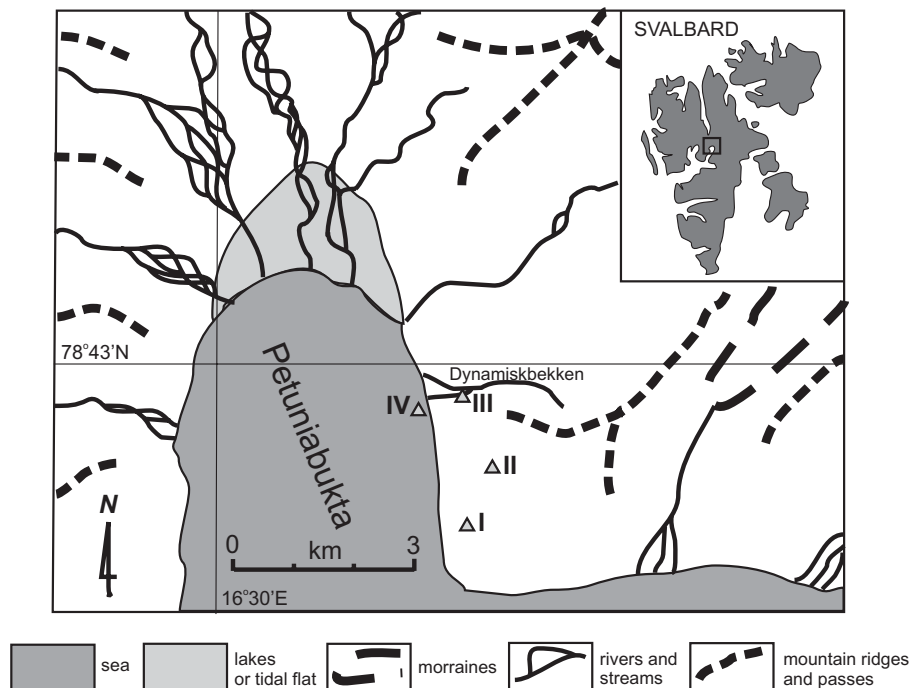


Fig. 2. Water sampling locations (I–IV) on the territory and in the vicinity of Dynamisk catchment (Central Spitsbergen).

men. Four rare ornithocrophilous plant communities have been distinguished in this area (Dubiel and Olech 1992).

The Dynamisk catchment (1.42 km²) is located at the foot of the Wordiekammen Massif (805 m a.s.l.) which has well-developed tali with various structural and textural features on its lower slopes (Kostrzewski and Zwoliński 2003). The foundation of the Dynamisk catchment consists of Carboniferous and Permian sediments belonging to the Gipshuken Group (Dallmann *et al.* 1999) dominated by carbonates. Above the tali there are several steep rock walls which give shelter and nesting sites for birds, in particular fulmars (*Fulmarus glacialis* L.) and glaucous gulls (*Larus hyperboreus* L.). The inaccessibility of the area and the isolation of the various bird colonies makes it difficult to estimate their total number. However, the colonies are large enough to influence the development of several plant communities.

Sampling. — Samples of surface water were collected in both catchments during the summer seasons (July, August, September) over two consecutive years (2001 and 2002). The sampling locations for both catchments were at the foot of the mountain slopes occupied by nesting birds. However, the streams flowing through the sampling areas also collect water from neighboring catchments.

Sampling locations are shown in Figs 1 and 2 (as points I–IV). All samples of surface water, which drained through the bird colonies, were subjected to basic preliminary physicochemical tests (temperature, pH and specific conductivity), followed by filtration with Millipore 0.45 μm membranes and thymol preservation. After the filtration process, samples of 1 dm^3 volume were stored at a temperature of 5–10°C in polyethylene bottles, which had been modified so as to prevent washing out from the polyethylene of some pollutants *e.g.* heavy metals. The bottles were transported for further analysis to the laboratory of Institute of Chemistry (University of Silesia in Katowice, Poland).

Sampling of calciferous rocks were taken close to water sampling locations. Samples of calcite from Fugle catchment were designated KF and MG, and those of dolomite and limestone from Dynamisk catchment, WB and WD.

Concentration of uric acid. — Uric acid ($\text{C}_5\text{H}_4\text{N}_4\text{O}_3$), represented by the concentration of urate ions, was determined by Dionex diode array detection (DAD) with an application of High Performance Liquid Chromatography (HPLC) method, using a Speedisk C_{18} solid-phase extraction method. To perform the extraction process, the sorbent was conditioned by the following reagents: 6 mL acetone, 6 mL methanol and 3 mL water. The analyzed 50 mL water sample was then passed through a prepared deposit; the sorbent was then dried for 20 minutes and, finally the accumulated components on the deposit were eluated. The extract was concentrated to the volume of 1 mL in a nitrogen stream and then alkalized. Then, the sample was analyzed using the HPLC/DAD method. The mobile phase in this analysis was a methanol-water-acetic acid mixture.

To determine the quantity of uric acid comparisons with standards were made. Triplicate samples were analyzed and mean values calculated. The accuracy of the determinations was $\pm 10\%$.

Stability of uric acid in water solutions. — The surface water samples (1L) were taken from various locations of the Fugle catchment and filtrated through a Millipore membrane ($\varphi = 0.45 \mu\text{m}$). A saturated solution of uric acid (10 mL, $T = 30^\circ\text{C}$, 0.9 mg of acid) was then added to each of the three samples. Prepared solutions were stored for 90 days at 4°C, and were analyzed every 30 days chromatographically.

Solubility of carbonate rocks. — The solubility of carbonate rocks was compared with that of analytically pure reagent of calcium carbonate *i.e.* one having the crystallochemical structure of calcite. Two samples (KF and MG) from the Fugle catchment and two samples (WB and WD) from the Dynamisk catchment were used to analyze the solubility of carbonate rocks. All samples underwent X-ray phase analysis using a Philips PW 1480 XRF X-ray diffractometer. Diffraction patterns of samples were recorded by using $\text{Cu K}\alpha$ radiation ($\text{Cu K}\alpha U = 40 \text{ kV}$, $I = 20 \text{ mA}$). In addition to the X-ray tests, thermogravimetric analysis of samples was also con-

ducted using a Perkin Elmer Thermal Analysis (Pyris) instrument. On the basis of the diffraction patterns, it was determined that, crystallochemically, the samples of rock from Fugle catchment (KF and MG) are nearly 100% pure calcite. These results were also confirmed by thermogravimetric analysis, which indicates that the composition of KF and MG rock samples are pure CaCO_3 . By contrast, analysis of diffraction patterns of rock samples from Dynamisk catchment (WB and WD) showed that their major component is dolomite with ~12% of silica (SiO_2) in the WD and ~7% of elemental carbon in the WB sample.

To analyze the solubility of carbonate rocks in both distilled water and aqueous solution of uric acid, fractions with diameters in the range 0.060–0.075 mm were collected from the crystallochemically determined samples. The solubility of the carbonate rock samples was examined by means of specific conductivity (SpC) measurements as a function of time. Results of the solubility of the rock samples in distilled water was then compared with the solubility in water solution of uric acid.

The experimental device used for those measurements included an electrode for the measurement of electrolytic conductivity, submerged in a 50 mL thermostatic vessel, placed on a magnetic stirrer, which provided continuous and uniform stirring. The electrode, together with a temperature detector, was connected to a multifunctional computer meter CX-742 manufactured by Elmetron, which registered changes of specific electrolytic conductivity during the dissolution of carbonate rocks. A thermostat maintained a constant temperature of 4°C ($\pm 0.5^\circ\text{C}$), which is the average ambient temperature of surface waters of non-glaciated catchments of Spitsbergen during the summer season.

Chemical analysis of solutions after the dissolution of carbonate rocks. —

The solutions, formed as a result of the dissolution of carbonate rock samples in distilled water and solutions of uric acid, were drained and analyzed for Ca and Mg by Flame Atomic Absorption Spectroscopy (FAAS) using a Solaar M6 spectrometer manufactured by TJA Solutions. The concentrations of HCO_3^- ions were determined by means of a titrimetric method (see Krawczyk 1996).

Results and discussion

Basic physicochemical parameters and values for uric acid concentrations, HCO_3^- and Ca^{2+} ions, in water flowing away from the non-glaciated Fugle catchment during July–September 2001, are shown in Table 2.

The uric acid concentration in surface waters of the Fugle catchment varied between 1.24 to 1.52 mg L^{-1} during the season, the mean concentration being 1.38 mg L^{-1} ($\pm 6\%$). The highest value was measured on 1st August, after the nesting period and during the season when the young birds learn to fly. Mean values of uric acid in 4 selected sites (with gps co-ordinates) in the Fugle and Dynamisk catch-

Table 2
Comparison of the determined physiochemical parameters of surface waters (sampling location II) in the Fugle catchment in 2001.

Date	T _{water}	pH	SpC	C ₅ H ₄ N ₄ O ₃	HCO ₃ ⁻	Ca ²⁺
	[°C]		[μS cm ⁻¹]	[mg L ⁻¹]	[mg L ⁻¹]	[mg L ⁻¹]
2001.07.09	3.5	7.74	99.7	1.29	64.0	20.5
2001.07.13	4.8	7.89	126.3	1.24	77.8	27.8
2001.07.20	5.0	7.66	125.3	1.29	71.7	25.5
2001.07.24	5.0	8.77	126.9	1.42	82.4	29.3
2001.08.01	4.2	8.09	147.8	1.52	77.8	27.6
2001.08.08	4.8	7.98	148.1	1.47	75.0	26.7
2001.08.14	4.0	8.13	157.9	1.48	82.4	29.5
2001.08.22	4.0	7.74	151.2	1.33	79.4	28.1
2001.09.12	2.5	7.63	154.2	1.41	61.0	21.7

Table 3
Comparison of average content of uric acid in selected sampling locations in the Fugle and Dynamisk catchments in the years 2001 and 2002.

Fugle catchment			Dynamisk catchment		
Sampling location	Uric acid concentration		Sampling location	Uric acid concentration	
	[mg L ⁻¹]	[mg L ⁻¹]		[mg L ⁻¹]	[mg L ⁻¹]
	2001	2002		2001	2002
site I	1.34 ± 0.13	1.28 ± 0.12	site I	0.70 ± 0.07	0.83 ± 0.08
N 77°00'27'' E 15°32'59''			N 78°40'43'' E 16°38'31''		
site II	1.33 ± 0.13	1.21 ± 0.12	site II	2.50 ± 0.25	3.70 ± 0.37
N 77°00'26'' E 15°33'32''			N 78°41'11'' E 16°38'05''		
site III	1.25 ± 0.12	1.74 ± 0.17	site III	1.40 ± 0.14	1.00 ± 0.10
N 77°00'18'' E 15°31'25''			N 78°41'39'' E 16°37'59''		
site IV	0.93 ± 0.09	0.63 ± 0.06	site IV	6.05 ± 0.60	7.50 ± 0.75
N 77°00'46'' E 15°29'29''			N 78°41'18'' E 16°35'22''		

Table 4
 Stability of uric acid in water solution from the Fugle catchment.

Sample	Sampling location	pH	SpC [mS cm ⁻¹]	Uric acid concentration		
				02.12.2002	03.01.2003	03.02.2003
			[mS/cm]	[mg L ⁻¹]	[mg L ⁻¹]	[mg L ⁻¹]
1	site II	7.08	139.4	0.21 ± 0.02	0.20 ± 0.02	0.20 ± 0.02
2	site III	6.83	181.9	0.24 ± 0.02	0.20 ± 0.02	0.20 ± 0.02
3	site IV	6.89	240.1	0.63 ± 0.06	0.61 ± 0.06	0.60 ± 0.06

ments during 2001 and 2002 are presented in Table 3. There is little spatial variation in the mean concentration of uric acid in surface waters of the Fugle catchment (0.63–1.74 mg L⁻¹), whereas in the Dynamisk catchment spatial variation in the concentration of uric acid is greater (0.70–7.50 mg L⁻¹). The results on Table 4 did not show any significant decrease in the initial concentration of uric acid.

Site IV was located in the estuary of Dynamisk stream and the sample includes water derived from the whole catchment. Therefore, it seems more reasonable to use the value of the uric acid concentration in that particular location for further calculations rather than calculate and use the average value from all sampling locations, because it is a real rather than a statistical value. The uric acid in the river catchment together with the birds' faeces dissolves in surface waters and dissociates more readily than carbonic acid (constant decomposition of uric acid is 3 grades higher than that of calcite). The uric acid reacts with the carbonate rocks of the catchment and dissolves them that is indicated by the laboratory results on the solubility of rock samples from these catchments. Solubility tests were conducted in distilled water and saturated solutions of uric acid at 4°C. For the purpose of these solubility tests, the KF and MG carbonate rock samples from Fugle area as well as WB and WD samples from the Dynamisk catchment were used. In addition, under the same conditions, the solubility of calcium carbonate (KS) was also analyzed. The results are shown in Fig. 3a and b.

Solubility isotherms presented in Fig. 3a and b show the interrelation between specific conductivity and time as well as the changes in concentration of calcium ions with respect to time. Figure 3a shows the solubility isotherms of limestone samples from the Fugle catchment (KF and MG) in distilled water (...+H₂O) and saturated solution of uric acid at a temperature 4°C (...+UA) contrasted to the solubility curves for calcite (KS+H₂O and KS+UA). Figure 3b shows the comparable solubility curve of limestone from the Dynamisk catchment (WB and WD). The calcite solubility curves in distilled water (KS+H₂O) and in saturated uric acid solution (KS+UA) are also shown. The curves in Fig. 3a and b show clearly that pres-

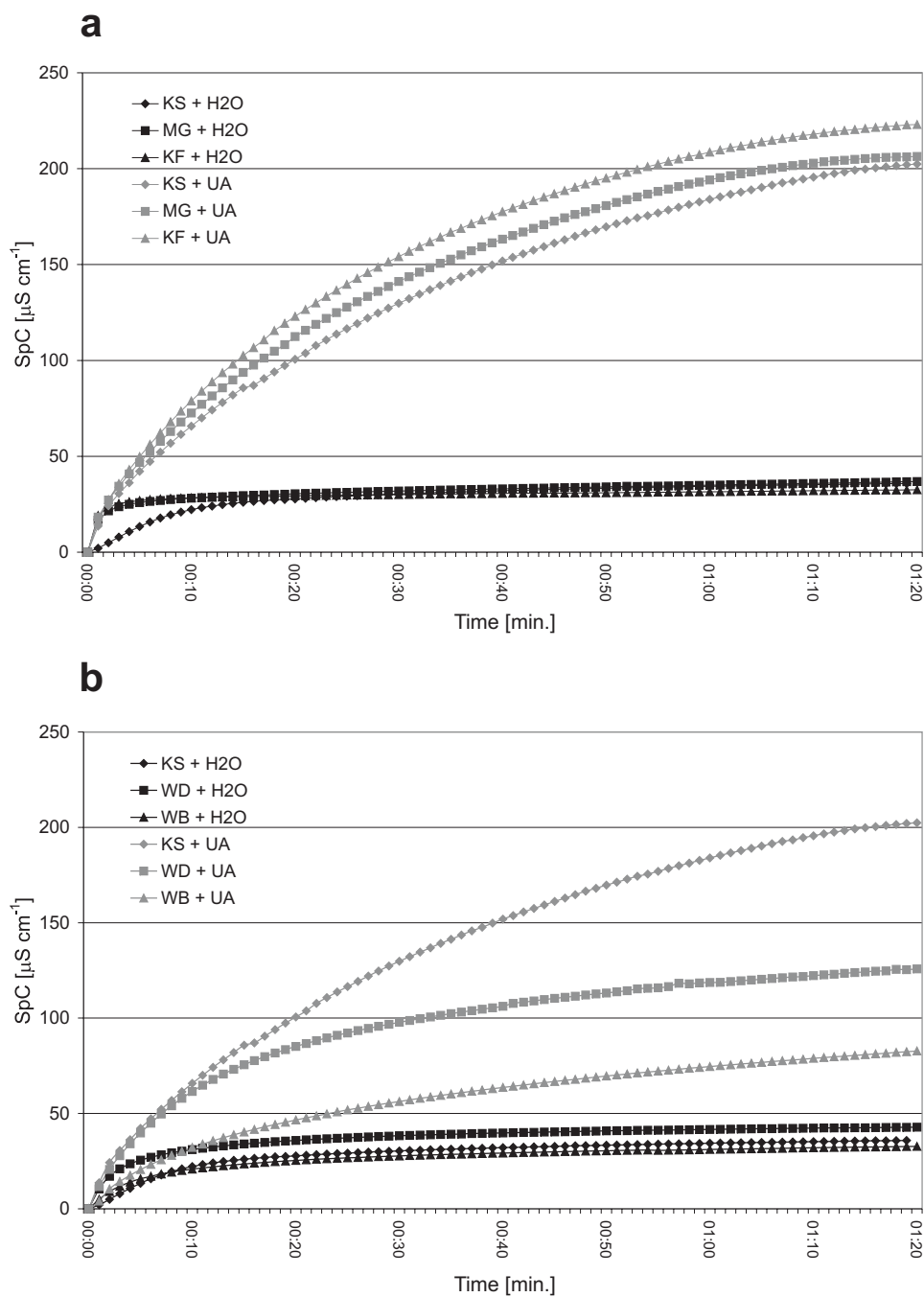


Fig. 3. Isotherms of rock samples solubility (a) from the Fugle catchment (MG, KF) and (b) from the Dynamisk catchment (WB, WD) as well as calcite (KS) in distilled water (...+H₂O) and solutions of uric acid (...+UA).

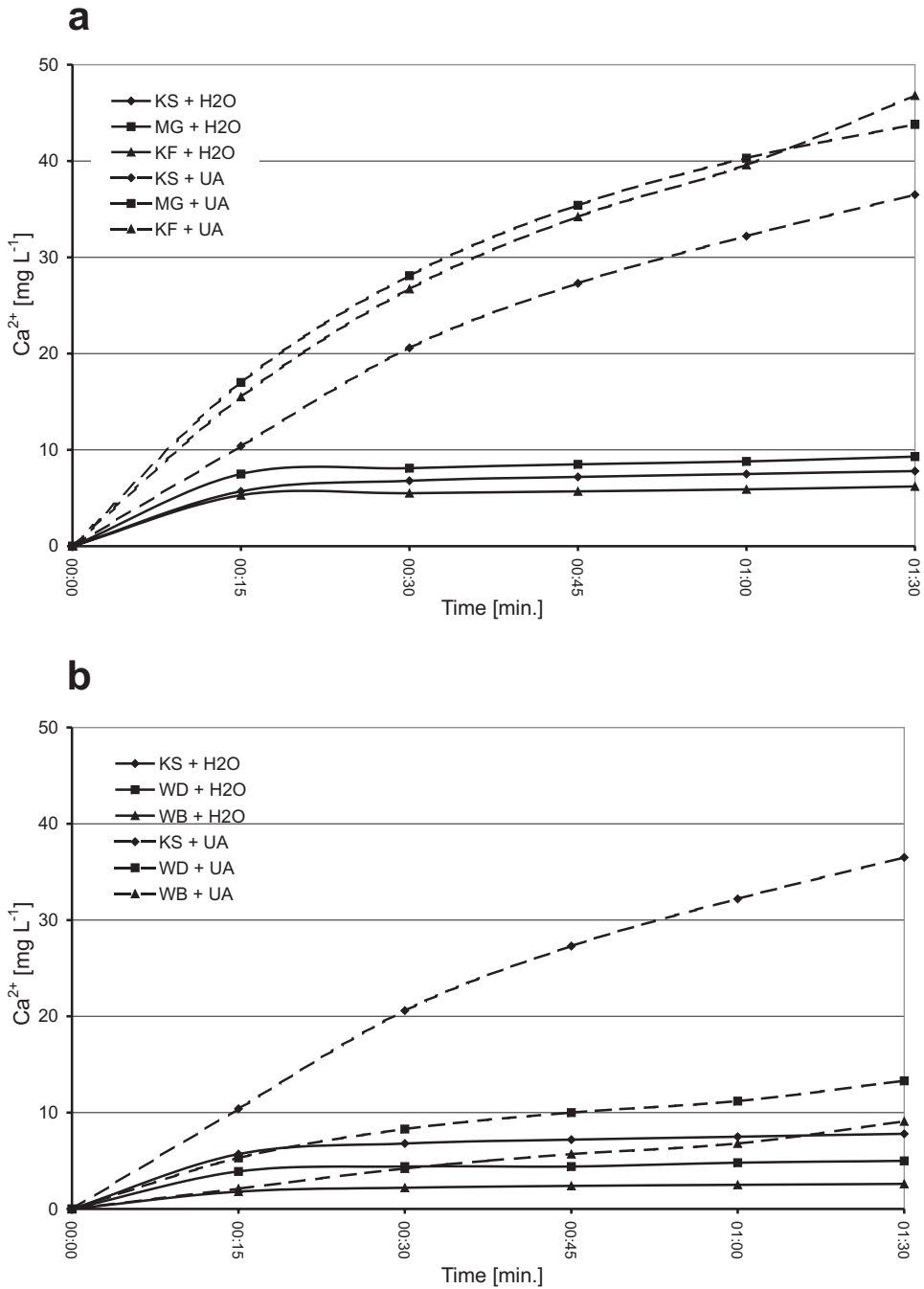


Fig. 4. Changes in Ca²⁺ concentration during the dissolution process of carbonate rocks (a) KF, MG in the Fugle catchment and (b) WB, WD in the Dynamisk catchment as well as calcite (KS) in water (...+H₂O) and solutions of uric acid (...+UA).

ence of uric acid increased the process of dissolution of all carbonate samples. The measured specific conductivity of solutions, formed during the dissolution process of carbonate samples from the Fugle catchment (Fig. 3a) and calcite, is significantly higher than the values obtained during dissolution in distilled water. By comparison, the carbonate samples from the Dynamisk catchment, which have a different chemical composition (mainly dolomite) and contain certain admixtures (silica, elementary carbon), show lower solubility in the solution of uric acid than the limestone from the Fugle catchment (comparison of curves MG+UA and KF+UA from Fig. 3a and WB+UA and WD+UA from Fig. 3b).

Figure 4a and b show the changes in calcium ion concentrations during the dissolution process of limestone samples from the Fugle (Fig. 4a) and Dynamisk (Fig. 4b) catchments as well as the dissolution process of calcite in distilled water and solutions of saturated uric acid. The curves are similar to those in Fig. 3a and b respectively.

Determination of the calcium urate solubility product. — The calcium urate obtained in the chemical reaction of uric acid and calcium hydroxide accords with the following equation:



Its chemical composition was determined by elemental and thermogravimetric analysis.

The value of the calcium urate solubility product was determined by measuring the electrolytic conductivity of its saturated water solutions. The determined numerical value is 1.6×10^{-8} , where $T = 4^\circ\text{C}$.

From the solubility product, the calcium ions and urate ions concentrations in saturated solution of calcium urate were calculated as follows:

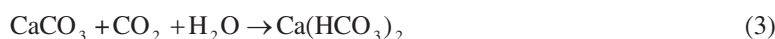
$$[\text{Ca}^{2+}] = 5 \text{ mg dm}^{-3}$$

$$[\text{C}_5\text{H}_4\text{N}_4\text{O}_3^{2-}] = 21 \text{ mg dm}^{-3}$$

Uric acid appears in water in two forms – enolic and ketonic, the latter being dominant (Fieser and Fieser 1958). Only the enolic form is subject to the dissociation process, with a dissociation constant of $K = 1.3 \times 10^{-4}$, which is higher by 3 orders than the dissociation constant of carbonic acid ($K = 4.3 \times 10^{-7}$). Consequently uric acid easily dissolves carbonate rocks, according to the following reaction:



The carbon dioxide formed in water solution causes further dissolution of carbonates according to the reaction:



The product of the reaction dissolves easily in water. Therefore, one mole of uric acid (168 g) dissolves 2 mole of carbon urate (200 g).

The role of uric acid in the dissolution processes which affect carbonate rocks. — According to Pulina *et al.* (2003), the mass of carbonate rocks dissolved by CO₂ present in the Fugle catchment (July–August 2001) is 2462 kg at the water outlet of the non-glaciated catchment (approx. 200,000 m³). The average concentration of urate ions during this period in Fugle waters is 1.38 mg dm⁻³. The total mass of dissociated form of uric acid was 1.38 mg dm⁻³ × 2 × 10⁸ dm³ = 276 kg, which according to Equations 2 and 3 has dissolved 328 kg of CaCO₃. Half of the mass (164 kg) of calcium carbonate is dissolved by CO₂ (Equation 2). Therefore, the total mass of dissolved carbonates is 2626 kg including 2462 kg with the participation of CO₂ (Equation 3) and 164 kg according to the Equation 2. Thus, the role of uric acid in the dissolution process of carbonates present in the ground of the Fugle catchment is 12.5% of the total mass of dissolved carbonates.

The volume of outlet from the Dynamisk catchment of Spitsbergen in the measuring period of 2002 was 198,815 m³ (Burzyk 2004) and the average concentration of calcium ions was 16 mg dm⁻³, which corresponds to 3181 kg of calcium ions in the catchment waters. With regard to the average uric acid concentration at site IV, the total mass of uric acid in catchment waters is 481 kg (2.42 mg dm⁻³ × 198,815 m³). Such a mass of uric acid implies the dissolution of 5728 kg of calcium carbonate, which is 7.2% of the total mass of dissolved calcium carbonate.

Concluding remarks

The dissolution of carbonate rocks is caused mainly by carbon dioxide present in water. The presence of CO₂ in water is related to numerous factors *e.g.* the reaction of uric acid with the geology of a catchment, which consists partly of carbonate rocks. We have demonstrated that the role of uric acid in the dissolution process of carbonate rocks is significant and in the Fugle catchment amounts 12.5%, whereas in the Dynamisk catchment, it is only 7.2%. This difference probably results from the different geological foundations of these two areas. In terms of the species and population, the seabird colonies of those two areas also differ considerably. Further the seabirds in these two areas have appreciably different diets. This may also result in different amounts of uric acid in their faeces. The uric acid present in the faeces enters to the surface waters mostly during rainfall. Its concentration is highest in these locations, due to the direct delivery to the environment. Uric acid precipitates from water solution when its concentration reaches 21 mg dm⁻³. The concentration of uric acid determined by us in surface waters was lower. However, this does not exclude the possibility of precipitation of urates in waters directly influenced by seabird colonies. The isolation of urates from the rest of the suspension material (*e.g.* the silica and humic acids which form in the tundra fertilized by birds) requires further investigation.

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