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CHEMICAL COMPOSITION OF INDIVIDUAL STORMS AS A FUNCTION OF AIR PARCEL TRAJECTORIES FOR THE PREDICTION OF ACID RAIN CHARACTERISTICS

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ABSTRACT

The object of the study is to investigate the effects of local industrial emissions on precipitation Chemistry in Northwestern British Columbia. In the study area in addition to general precursors to acid rain such as Sulphur Dioxide (16 tonnes per day), the presence of Hydrogen Fluoride (2.18 tonnes of total Fluoride per day) presents a unique situation in Western Canada. In order to assess the impact of SO_2 and HF emissions on pH, event precipitation samples were collected and analysed. The data showed that the fluoride concentration in ambient air decreased with increased precipitation. It also showed that the acidity and fluoride concentration in rain were higher in the summer than in other seasons, the fluoride wet deposition rate was at a minimum in summer due to the lower rainfall. Furthermore, the comparison of storm trajectories with observed ionic loading has offered an opportunity to qualitatively assess pollution received by rain water during storms from local individual industrial sources as well as distant natural and other sources.

INTRODUCTION

Acid rain measurements in British Columbia has been monitored at eight stations by the Atmospheric Environment Service (AES) since April 1977 as part of the Canadian Network for sampling precipitation (CANSAP). The CANSAP samples were monthly averages made up from a composite of individual events with quite different air trajectories and air mass histories and therefore do not fully explain certain local emission effects on rain water chemistry. A program to provide a data base for the B.C. Coast by sampling individual storm events was introduced in 1980. The network consisted of five sites in the northwest of B.C., Prince Rupert-Terrace-Kitimat area and one site on the Vancouver Island, Port Hardy. The acid rain monitoring sites are shown in Figure 1.

The main object of the study is to investigate, with and without the effects of local industrial emissions on precipitation chemistry of individual storms on the west coast of British Columbia.

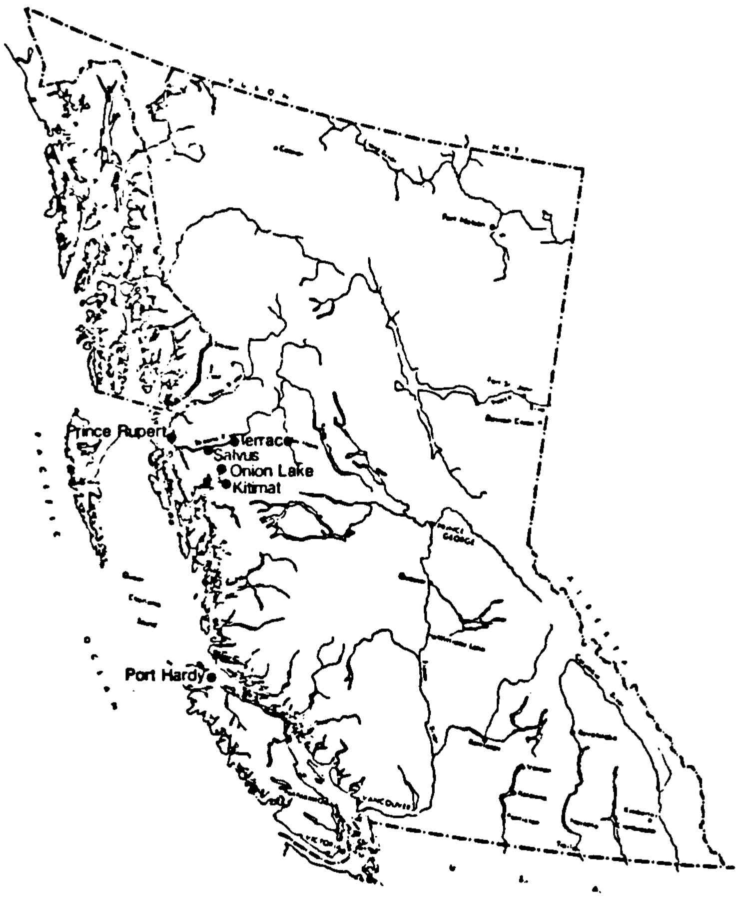


Figure 1
British Columbia showing Acid Rain Monitoring Stations

EMISSIONS

In the Kitimat area the Aluminum Smelter and Kraft Pulp Mill are two main sources of emissions. For the period July 1980 to June 1981, the emissions from the smelter averaged about 2.18 tonnes of total fluoride per day (1.57 tonnes of gaseous fluoride and 0.61 tonnes of particulate fluoride) and 13.1 tonnes per day of sulphur dioxide. The Kraft pulp mill emissions amount to 1.2 to 2.0 tonnes per day of sulphur dioxide, and less than 1.0 tonne per day of organic sulphur compounds.

In the Port Hardy area the sulphite pulp mill is the main source of sulphur dioxide emissions which is about 10 tonnes per day.

AMBIENT MONITORING NEAR SMELTER

FLUORIDE

Fluoride was measured by lime plate [1] method. In the lime plate method, the lime plate was exposed to the atmosphere for 30 days, then analyzed for fluoride content. This method measures only gaseous fluoride and has been used as a qualitative index of the gaseous fluoride levels. Results were expressed as fluoridation rate in $\mu gF/(cm^2.day)$.

In order to indicate the concentration of fluoride in the ambient air with distance in the northern sector from the smelter, data from eleven stations are presented in Table I. It is noted from the fluoridation index data that the index decreased with increasing distance from the smelter, although the decrease was sharper after a distance of 3.2 km north of the smelter.

TABLE I
FLUORIDATION INDEX IN KITIMAT, B.C., MEASURED NORTH OF ALCAN*
RESULTS IN $\mu gF/(cm^2.d)$

Serial Number	Site Name	Distance(N) w.r.t. Alcan Mill, km	Average F Index	Maximum F Index	Minimum F Index	No. Of Samples	Period
1	North Alcan Fence	1.28	1.109	2.295	0.089	24	Mar. 76 - Jun. 78
2	C.N. Crossing Pole	3.20	0.138	0.354	0.009	19	Nov. 76 - Jun. 78
3	Standard Station	5.20	0.040	0.185	0.005	19	Nov. 76 - Jun. 78
4	Doc's Cartage Pole	5.60	0.050	0.130	0.010	18	Nov. 76 - Jun. 78
5	Municipal Works (Alcan)	5.60	0.020	0.040	0.0001	22	Jul. 75 - Mar. 78
6	Saunders	6.40	0.037	0.123	0.005	19	Nov. 76 - Jun. 78
7	Three Mile	7.60	0.012	0.038	0.005	16	Nov. 76 - Jun. 78
8	Six Mile	21.20	0.052	0.151	0.005	14	May 77 - Jun. 78
9	Nine Mile	28.80	0.046	0.122	0.005	13	May 77 - Jun. 78
10	Iron Mt.	31.20	0.025	0.048	0.005	7	Jun. 77 - Jun. 78
11	End of Valley	48.00	0.013	0.040	0.005	17	Nov. 76 - Jun. 78

Ref: "Assessment of Ambient Air Quality in Kitimat, B.C." by B.B. Manna

SULPHATION RATE

The sulphation rate provides a rough estimate of sulphur dioxide concentration in ambient air. The sulphation rate was determined by using the candle method [2]. This consisted of exposing a lead peroxide coated procelain cylinder for a month. After exposure, the coating was analyzed in the laboratory for its sulphate content. Results were expressed as sulphation rate in mg $SO_3/(100\ cm^2.day)$.

The sulphation data collected at four stations during the period July 1975 to March 1978 has been summarized in Table II. It is noted from the summary that the sulphation rate at most of the stations was well within the specified British Columbia or Ontario standard of 0.5 and 0.7 mg $SO_3/(100\ cm^2.day)$, respectively. Also the sulphation rate decreased with distance from the smelter.

TABLE II

SULPHATION RATES FROM ALCAN STATIONS WITH KITIMAT AREA
RESULTS IN mg SO_3/(100 cm^2day)

STATION AND EQUIS NUMBER	TOUR BUILDING 0435040	HYDRO SUB STATION 0435035	POLLUTION CONTROL CENTRE 0435037	MUNICIPAL WORKS 0435036
Distance & direction from Alcan	1.2 km, N.W.	3.2 km, N.W.	4 km, N.E.	5.6 km, N.
Period	Jul. 77 - Mar. 78	Jul. 75 - Mar. 78	Jul 75 - Mar. 78	Jul. 75 - Mar. 78
Average	0.27	0.15	0.02	0.04
Number of values	9	33	23	18
Number exceeding a value of 0.7*	1	1	0	0
Period	1979	1979	1979	1979
Average	0.29	0.17	0.14	0.05
Number of values	12	12	12	12
Number exceeding a value of 0.7* mg SO_3/(100 cm^2.day)	0	0	0	0

• The Province of Ontario Standard

PRECIPITATION

Precipitation normals [3] for the period 1941 to 1970 were available from the Federal Stations: Prince Rupert, Terrace Airport, Kitimat and Port Hardy Airport. The total precipitation at these stations per year were 2414, 1301, 2826 and 1730 mm, respectively. The wettest month at Kitimat, Prince Rupert, Port Hardy and Terrace was October with 460, 360, 250 and 232 mm of precipitation and in summer months precipitation has been substantially less. While snowfall at Prince Rupert and Port Hardy was low at about 100 cm, Kitimat and Terrace Airport averaged about 400 cm, most winters.

PRECIPITATION EVENT SAMPLING

PORT HARDY

At Port Hardy an event precipitation sampling site was located at Port Hardy Airport. About 35 km south of the Port Hardy precipitation monitoring site there is a sulphite pulp mill. Ten events data obtained by the Ministry of Environment while the mill was operating was compared with Nikleve [4] data when the mill was shut down. The date has been presented in Table III. It can be seen from this data that the concentration of excess sulphation was more during mill operations than when the mill was shut down. The background pH of rainwater at this site was about 5.3

KITIMAT

The smelter staff collected rain samples at the Pollution Control Centre site, 4 km NNE of a smelter using the Sangamo automatic rain sampler.

TABLE III

PORT HARDY EVENT PRECIPITATION DATA

Parameters mg/l	pH	Ca^{2+}	Mg^{2+}	NH_4^+	Na^+	C/-	SO_4^{2-}	NO_3^-	Excess SO_4^{2-}
Mill Operating Sept. 1980 to Nov. 1981 (10 Events)	4.73-5.81	0.097	0.093	0.079	1.042	1.55	1.2	0.39	0.98
Mill Closed March 1982	5.3	0.054	0.164	0.038	1.03	1.90	0.4	0.11	0.13

The company has measured pH and F^- in precipitation. The relationship between pH and F^- in event precipitation samples is illustrated in Figure II.

The low level roof top emissions of F^- and SO_2 from the smelter may be removed from the atmosphere by wet deposition. Washout of F^- by rainfall is relatively easy because of the high solutility of F^- in rainwater and this is reflected in the inverse relationship between pH and F^-, Figure II.

RAIN CHEMISTRY OF INDIVIDUAL STORMS AS A FUNCTION OF AIR PARCEL TRAJECTORY

In order to delineate the variability associated with individual storms, nine precipitation events were studied on a storm by storm basis from September 1980 to November 1981. For each storm five samples were collected in the Prince Rupert-Terrace-Kitimat area and their ionic composition were determined.

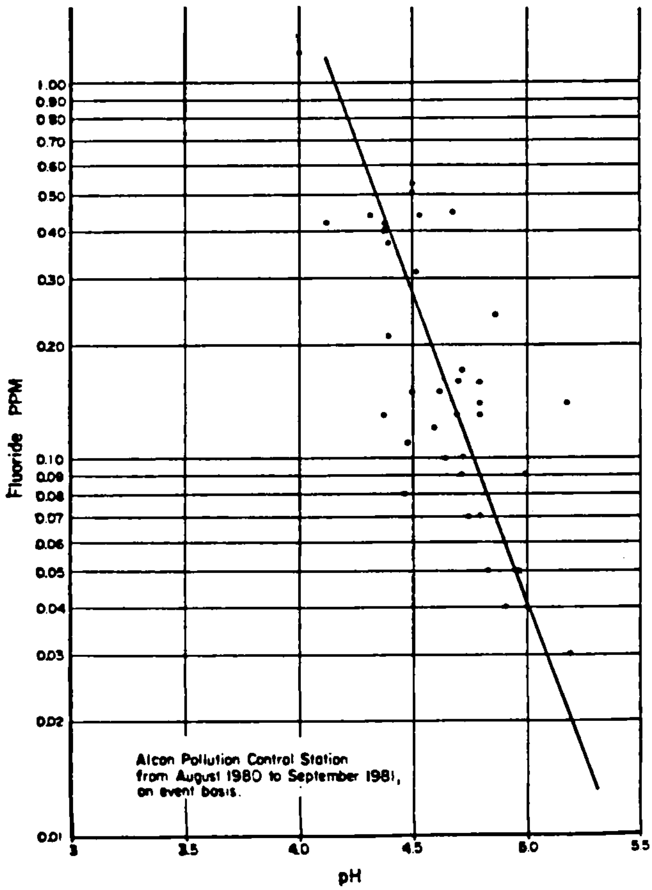
To trace the origin of the air parcel associated with each precipitation event back trajectory analysis was done. Tracks of air parcels were estimated for 24 hours in increments of 12 hours. This allows one to examine for possible correlation between the chemistry of rain sample and the meteorological parameters such as the geographical position of the storm track, its orientation and the speed of movement of the storm. (Since time interval is fixed at 12 h, the speed of movement of storm is proportional to the length of the storm track in that time interval). The back trajectory data of 9 storms are summarized in Table IV and representative storm tracks are presented in Figure III.

The visual observation of 24 h air mass trajectories presented in Figure III indicates that storm trajectories can be grouped into three categories: (1) over water, (2) over land, and (3) other unique trajectories, and they can be compared with respective influences on the acidity in the precipitation.

1. ACID CONTRIBUTION FROM STORM TRAJECTORIES OVER WATER

The synoptic weather maps for September 3 and 18, 1980, and September 9, 1981, i.e., Case 1, 2 and 7 presented in Figure III, showed winds

FIGURE II FLUORIDE IN RAINWATER vs pH



predominantly south-southwesterly over the Pacific. The observed rainfall of Terrace for these cases was 25, 20 and 8.2 mm, respectively. The wind speeds for Cases 1, 2 and 7 were 15, 6 and 24 knots respectively. A comparison of chemical constituents for these three cases indicates:

a. The pH value for Case 2 at Terrace and Onion Lake was about 5.9 while the value for Case 1 and 7 ranged between 5.01 and 5.47. This indicates that the storm with minimum speed (case 2) had slightly buffered rain when contrasted with the other two cases.
b. The fluoride concentration in Case 7 rain samples at Onion Lake and Terrace was 0.07 and 0.06 mg/l respectively, considerably greater than in the Case 1 and 2, which had fluoride concentration of <0.04 mg/l. This indicates that the storm with minimum rain had a higher fluoride concentration.

TABLE IV

SUMMARY OF TERRACE STORM BACK TRAJECTORY DATA

Case Number By Season				Period	Length of Track Over Land In Percent (in map units, cm)†	Length of Track Over Ocean In Percent (in map units, cm)†	Wind at 850 mb		Precipitation mm
W	S	S	F				Speed In Knots	Time/Date Observed	
4				February 18-19, '81	92 (11.0 cm)	8 (1.0 cm)	42	0400/19 Feb	8
	5			May 13-15, '81	100 (3.8 cm)	0 (0.0 cm)	17	0400/14 May	10
		*6		August 14, '81	0 (0.0 cm)	100 (6.2 cm)	7	1600/14 Aug	Trace
			1	September 3-4, '80	10 (1.0 cm)	90 (9.0 cm)	15	0400/03 Sept	
			2	September 18-19, '80	29 (1.5 cm)	71 (3.7 cm)	6	0400/18 Sept	20
			3	November 4-5, '80	71 (6.4 cm)	29 (3.0 cm)	61	0400/05 Sept	21.4 (4th) 37.0 (5th)
			7	September 9, '81	12 (1.5 cm)	88 (10.7 cm)	24	1600/10 Sept	8.2
			*8	October 26-27, '81	0 (0.0 cm)	100 (12.5 cm)	45	1600/28 Sept	13.0
			9	November 9-12, '81	28 (3.0 cm)	72 (9.1 cm)	20	0400/12 Nov	49.0

* Track 6 and 8 did not touch Terrace

† Scale of map, 1 cm = 94 cm

2. ACID CONTRIBUTION FROM STORM TRAJECTORIES OVER LAND

The storm of November 4 (Case 3), was characterized by strong winds, 61 knots. The flow was southeasterly and over land for the most part. The rainfall at Terrace was 21 mm.

The storm for Case 5, which occurred on May 13, was one with moderate winds. The storm moved very sluggishly over land, see Figure III. About 10 mm of rain fell over Terrace.

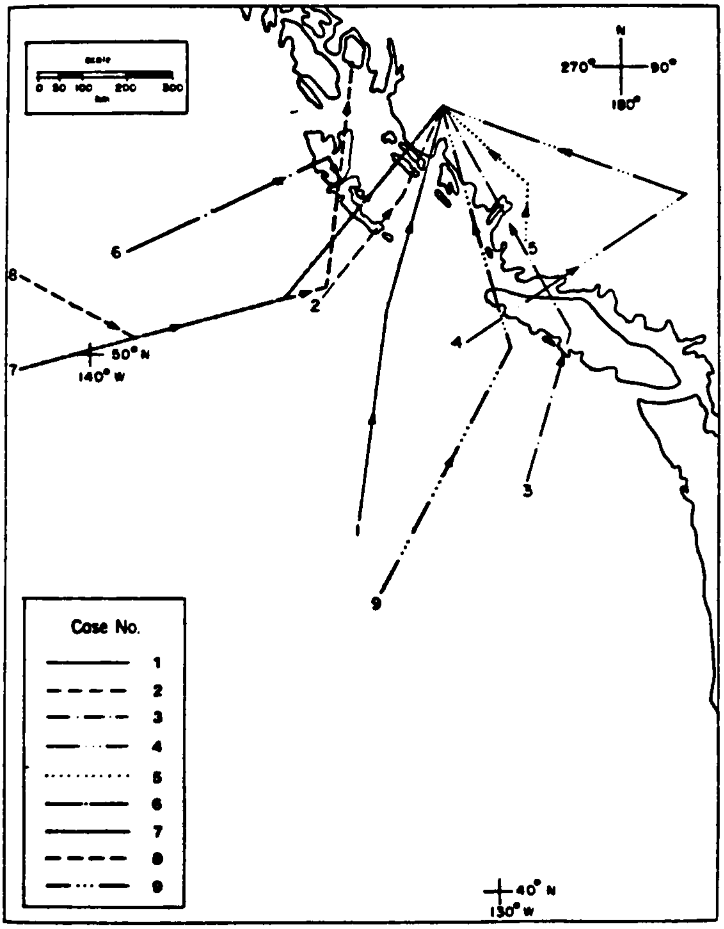
The chemical composition of rain samples collected at Kitimat, Onion Lake, Terrace, Prince Rupert and Salvas Camp are summarized in Table V. The data indicates that rain samples associated with light rainfall, 10 mm, and with the slower storm over land, which passed over Alcan, deposited more fluoride with rain samples collected in the Kitimat Valley, (Kitimat, Onion Lake and Terrace) whereas Skeena Valley samples, (Prince Rupert and Salvus camp) showed background fluoride levels i.e. 0.04 mg/l.

The results of excess sulphate are presented in Table V. The data suggests that 2 mg/l of Kitimat precipitation and 1.3 mg/l of Terrace precipitation has excess sulphate, likely of industrial origin. A similar excess SO_4^{2-} concentration was observed in Prince Rupert precipitation. Furthermore, the total acidity in the Kitimat Valley precipitation was noted to be higher (30 to 124 µeq/L) than in the Skeena Valley (18 to 30 µeq/L).

3. ACID CONTRIBUTION FROM STORM TRAJECTORIES WITH UNIQUE FEATURES

In this category the storm system of Case 4 represents a system with over land flow. This case is unique. On February 18, the storm passed over north Vancouver Island and into the drier Okanagan Valley. It then drifted toward Terrace, see Figure III. During its passage, the storm appears to have picked up aerosols such as Ca^{+2} of terrestrial origin which had a buffering effect on the rain samples collected at Kitimat and Terrace, see Table VI.

FIGURE III
BACKWARD 24 HOUR (850 mb) TRAJECTORIES FOR TERRACE



The rain samples collected on February 19/20 showed depressed pH due to lack of terrestrial components such as Ca^{+2} see Table VII.

The variations observed in the two data sets are probably due to terrestiral effects in the first data set, and local industrial influence observed in the second data set. The increase in fluoride and aluminum in the second data set was due to washout of local (Alcan) pollution in the ambient air.

CONCLUSIONS

The study examines the emissions that contribute to acidity of precipitation in the Kitimat and Port Hardy area. From July 1980 to June 1981, the Aluminum Smelter at Kitimat emitted 2.18 tonnes of total fluoride per day (1.57 tonnes of gaseous fluoride and 0.61 tonnes of particulate

TABLE V

CHEMICAL COMPOSITION OF RAIN SAMPLES COLLECTED IN NORTHWEST, B.C. WHEN STORM TRACKS WERE OVER LAND

Station	Kitimat		Onion Lake		Terrace		Prince Rupert		Salvus Camp	
Case	3	5	3	5	3	5	3	5	3	5
Parameter										
pH	5.9	4.5	4.8	4.9	5.3	4.6	5.5	5.2	4.9	-
SO_4^{2-} mg/l	1.9	2.1	0.9	0.7	1.3	1.4	<0.5	1.6	0.5	-
NO_3^- mg/l	0.2	0.5	0.09	0.4	0.1	0.7	<0.1	0.4	0.13	-
F^- mg/l	0.07	1.2	<0.04	0.05	0.04	1.1	<0.04	<0.04	<0.04	-
Cl^- mg/l	0.6	<0.5	<0.5	<0.5	<0.5	0.7	0.5	0.5	<0.5	-
Ca^{2+} mg/l	0.4	0.19	<0.02	0.05	<0.02	0.2	0.02	0.14	<0.02	-
Na^+ mg/l	0.7	0.5	0.1	0.2	0.1	0.6	0.2	0.6	0.1	-
Cation Anion	1.0	0.97	1.29	0.50	0.28	0.89	-	0.8		
Excess SO_4^{2-}	1.8	2.0	0.8	0.6	1.2	1.3	0.4	1.5	0.4	
Total Acidity μeq/l	30	124	74	50	25	92	18	32	28	-
Precipitation	-	-	-	-	21	10	-	-	-	-

Note: Case 3, November 4-5, 1980
Case 5, May 13-15, 1981

TABLE VI

Government Stations	Period	pH	Ca^{+2}	Na^+	SO_4^{2-}	Cl^-	F^-	Al
		mg/l						
Terrace	Feb. 18/19	5.8	0.21	0.3	1.9	<0.5	<0.04	<0.02
Kitimat	Feb. 18/19	7.0	1.75	3.0	6.0	2.1	<0.04	0.05

TABLE VII

Government Stations	Period	pH	Ca^{+2}	Na^+	SO_4^{2-}	Cl^-	F^-	Al
		mg/l						
Terrace	Feb. 19/20	5.4	<0.02	0.1	1.2	<0.5	<0.04	<0.02
Kitimat	Feb. 19/20	4.5	0.07	0.4	1.8	<0.5	0.69	0.14

fluoride), and 13.1 tonnes of sulphur dioxide per day. The pulp mill emissions at Kitimat were about 2 tonnes per day of sulphur dioxide, less than 1 tonne per day of organic sulphur compounds.

The sulphur dioxide emissions from the sulphite pulp mill near Port Hardy amount to about 10 tonnes per day.

The event precipitation data shows that the pH at Kitimat (Tour Building Site) ranged between 4.4 to 7.2, Onion Lake 4.8 to 5.9, Terrace Airport 5.1 to 6.0, Salvus Camp 4.7 to 5.6 and Prince Rupert 4.5 to 5.7. The highest pH noted at Kitimat, Tour Building site, would seem to be an anomally which can only be explained by assuming that the Kraft Mill particulate emissions appear to contribute a buffering influence on rain at this site. However, this influence was not felt at the Kitimat Pollution Control site since pH at this site was lower (4.3 to 4.9) than the Tour Building site.

The results show that the Port Hardy site is influenced by emissions from the sulphite mill. When the mill was not operating pH of rainwater at this site was found to be 5.3.

The comparison of storm trajectories with observed ionic loadings has offered a unique opportunity to qualitatively assess pollution received by rainwater during storms from local industrial sources as well as distant, natural and other sources.

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