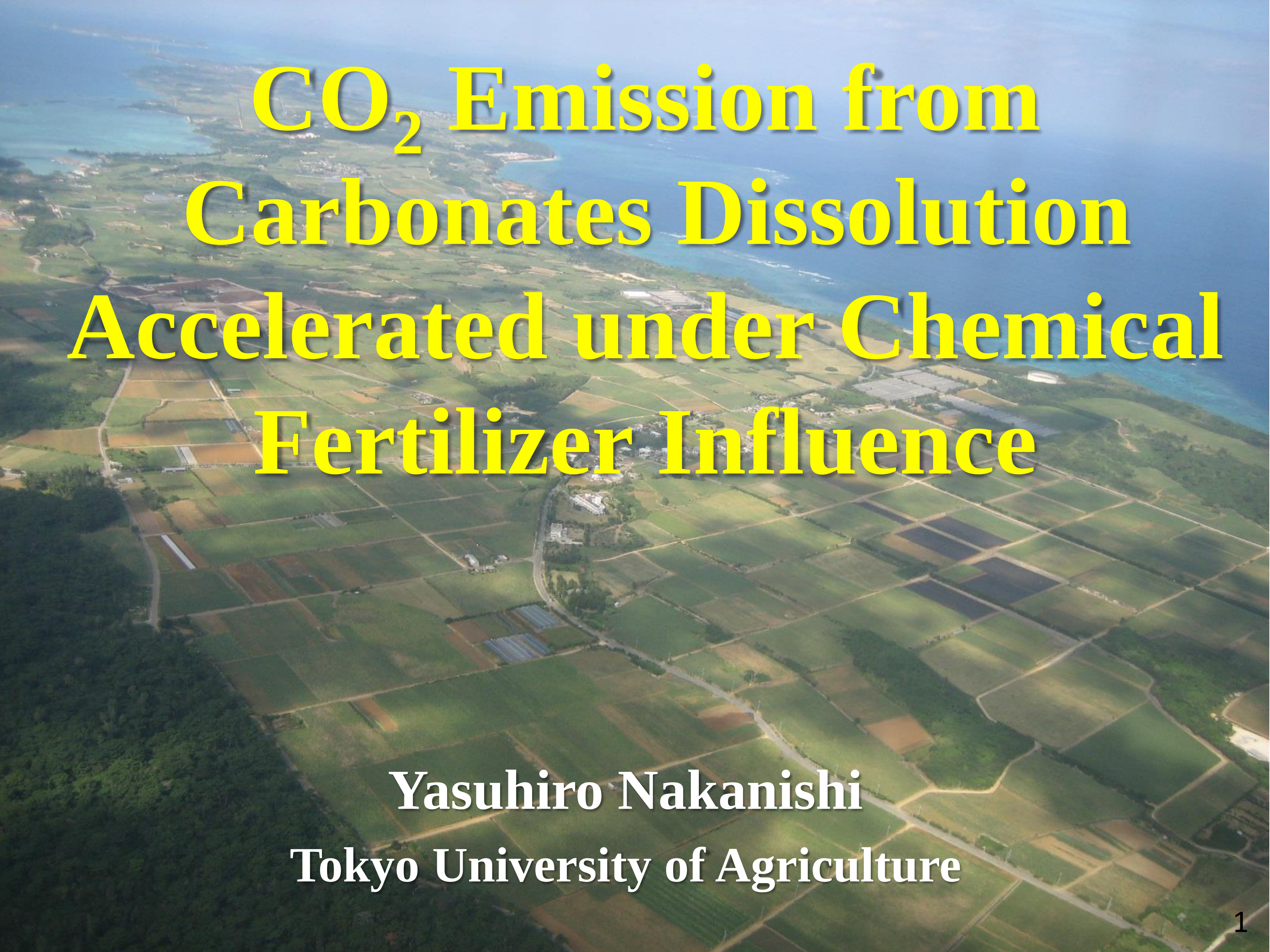

CO_2 Emission from Carbonates Dissolution Accelerated under Chemical Fertilizer Influence

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Contents of Presentation

Aim: To show that the modern agriculture can promote CO_2 emission from carbonates, such as limestone, under chemical fertilizer influence.

Why carbonates ?: Carbon amount in carbonate rocks in the world is thought not to be negligible in carbon balance.

Case study on CO_2 emission from carbonates: Coral islands in Okinawa, south of Japan.

Background of the emission: Inadequate application of chemical fertilizer to sugarcane in the islands.

Introduction:
Carbon amount on the earth

Table Carbon amount on the earth.

	$\times 10^5$GtC
Air	0.01
Saline and fresh water	0.35
Living organisms, Undecomposed organic matter	0.04
Carbonates	490.91
Organic matter in sediments	68.18
Coal, coal oil	0.07

Source: Kitano (1990)

Carbon on the earth is mostly (ca. 90 %) included in carbonates.

(e.g. Ford and Willians,1989; Gaillardet *et al.*,1999).

Introduction:
Distribution of carbonates in the world

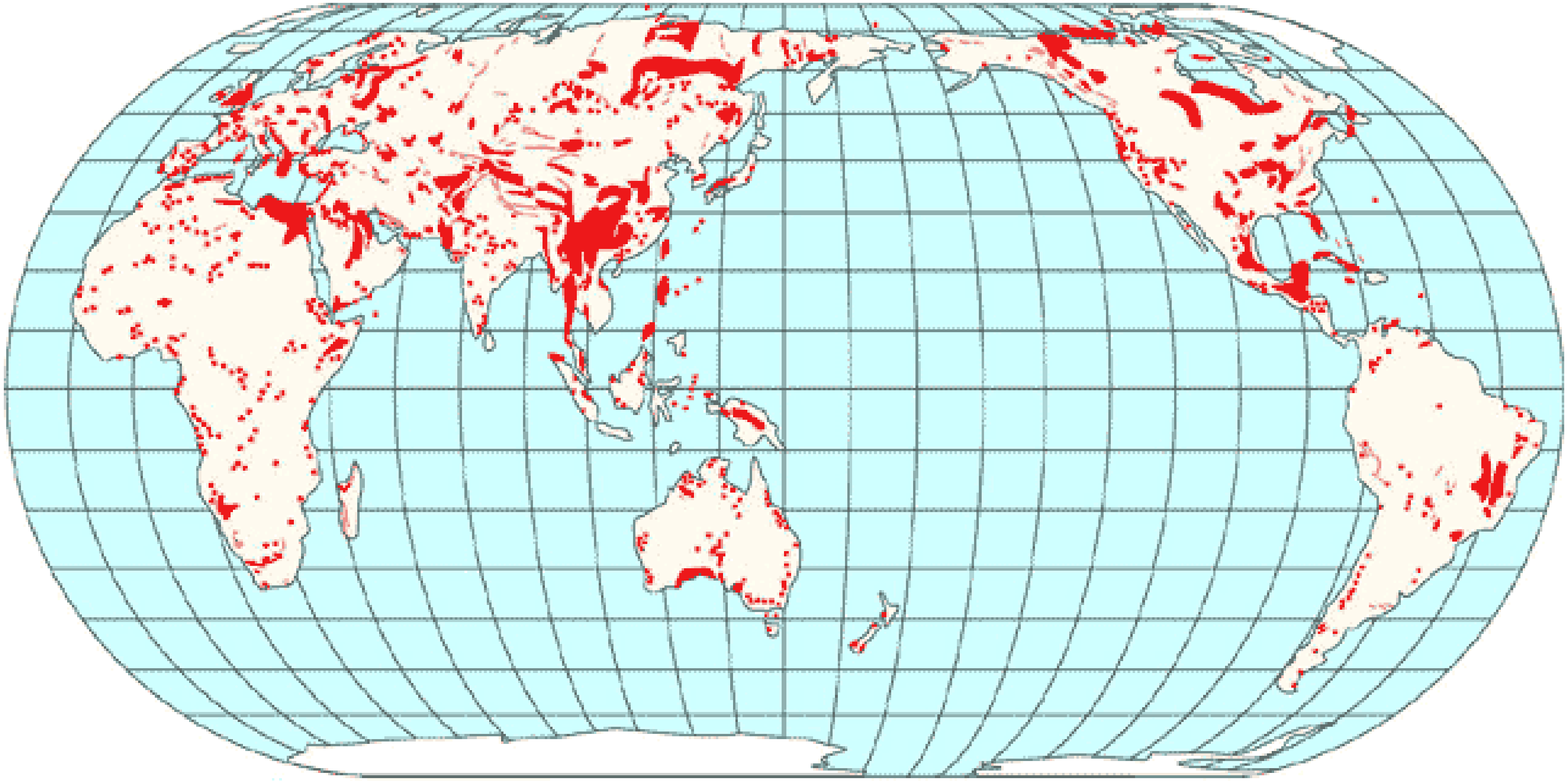


Fig. 1 Distribution of carbonate rocks in the world (red in color).
Source: Kono (2004)

Total area of carbonate rocks occupies ca. 11 % of total land of the earth. (Ford and Williams,1989).

Introduction:
Natural dissolution and formation of carbonates

Dissolution of carbonates:

Carbonates are dissolved by water reacted with CO_2 in air and derived from respiration as the formula (1).

$$Ca_{(1-x)}Mg_xCO_3 + CO_2 + H_2O \rightarrow (1-x)Ca^{2+} + xMg^{2+} + 2HCO_3^- \cdots (1)$$

Formation of carbonates:

Carbonates are formed by biological fixation and sedimentation in sea as the formula (2)

$$(1-x)Ca^{2+} + xMg^{2+} + 2HCO_3^- \rightarrow Ca_{(1-x)}Mg_xCO_3 + CO_2 + H_2O \cdots (2)$$

It is recognized that the reaction (1) and (2) have a good balance.

Introduction:
Anthropogenic dissolution of carbonates

In agricultural area formed by carbonate rocks in the south-west of France,

Perrin *et al.* (2008) have reported a possibility that carbonates are dissolved by H^+ derived from nitrification of ammonia in ammonium nitrate and thereby CO_2 is emitted, based on river water analysis, as the formula (3) and (4).

$$NH_4NO_3 + 2O_2 \rightarrow 2NO_3^- + H_2O + 2H^+ \text{--- (3)}$$

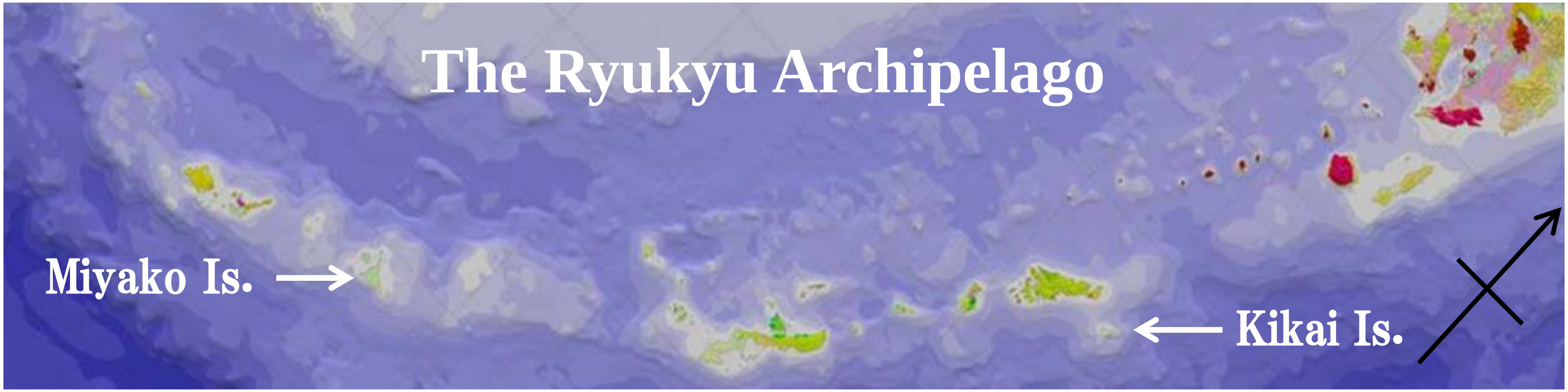
$$Ca_{(1-x)}Mg_xCO_3 + NH_4NO_3$$
$$\rightarrow (1-x)Ca^{2+} + xMg^{2+} + 2NO_3^- + 2H_2O + CO_2 \text{ --- (4)}$$

Other examples

- Acid rain can promote carbonates dissolution (Yoshimura and Nakamura, 1990).
- Decline of neutralization capacity by enriching negative ions can promote carbonates dissolution (Collins and Jenkins,1996; Pacheco *et al.*,2002).

Introduction:
Area formed by carbonate rocks in Japan

In Japan, the area formed by carbonate rocks occupies 0.4 % of the land area and is mostly located in the Ryukyu Archipelago.



- **The land area on the islands has been broadly cultivated since they have a flat and low-lying topography.**
- **Groundwater of the islands are polluted mainly by nitrates derived from chemical fertilizer applied to sugarcane, the main crop there** (e.g. Nakanishi, 2000).

Experiments conducted on:
CO_2 emission from carbonates of the coral islands

Hypothesis

In the agricultural area, nitrogenous chemical fertilizer

1) **Accelerates carbonates dissolution**
2) **Promotes CO_2 emission in the chemical reaction**

Study areas

Kikai Is. in Kagoshima Pref. and Miyako Is. In Okinawa Pref.

Study contents

Exp. 1: verification in groundwater chemistry
Exp. 2: clarifying relationship between CO_2 concentration at spring mouth and groundwater component
Exp. 3: verification by a model test using soil columns
Exp. 4: verification by an *in-situ* test in sugarcane field

Experiment 1: Inspection in groundwater chemistry

Aim

To inspect possibility of carbonates dissolution and CO_2 emission in agriculture area formed by carbonate rocks under chemical fertilizer influence.

Method for groundwater inspection

Object area: Agriculture and forest area on Kikai Is. and Miyako Is.

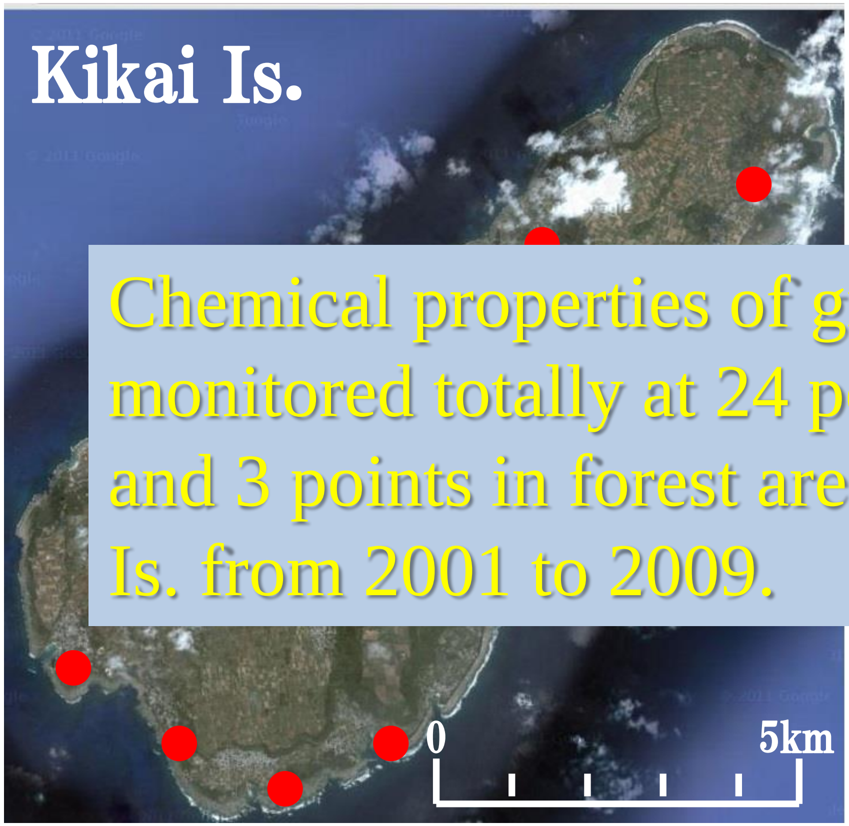
Period: From Jan. 2001 to Dec. 2009

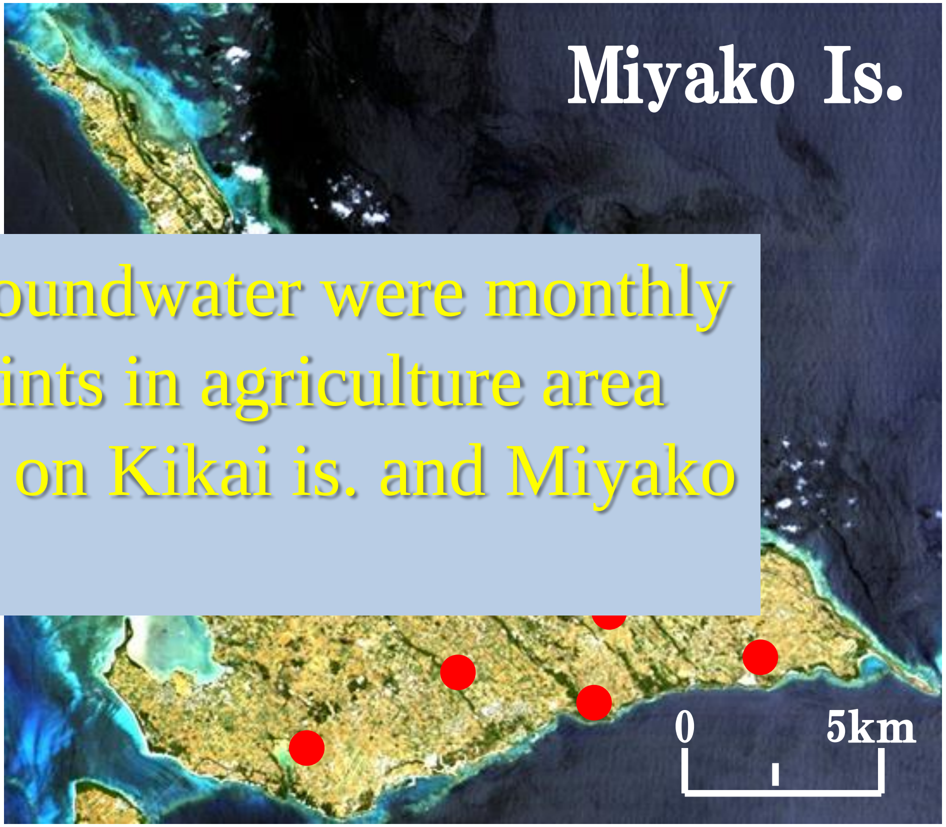
Sample collection: Once a month (n = 108)

Survey items: 1)Concentrations of H^+, Na^+, NH_4^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_2^-, NO_3^-, SO_4^{2-},and HCO_3^- ; 2) Sic (Saturation index of HCO_3^- to carbonates dissolution) ; 3) $P\text{co}_2$ (CO_2 partial pressure in GW)

$$\mathrm{SIc} = \log\left[\frac{\mathrm{K_2[Ca^{2+}][HCO_3^-]}}{K\mathrm{sp[H^+]}}\right] \qquad P\mathrm{co_2} = \frac{\mathrm{[H^+][HCO_3^-]}}{K_0K_1}$$

Experiment 1:Inspection in groundwater chemistry





Chemical properties of groundwater were monthly monitored totally at 24 points in agriculture area and 3 points in forest area on Kikai is. and Miyako Is. from 2001 to 2009.

Groundwater samples had been collected from 11 points in the agricultural area and 3 points in the forest area.

Groundwater samples had been collected from 13 points in the agricultural area

Fig. A typical geological cross section on Miyako Is. formed mainly by limestone.

The Ryukyu Limestone layer: Very high permeability

The Shimajiri Mudrock layer: Very low permeability

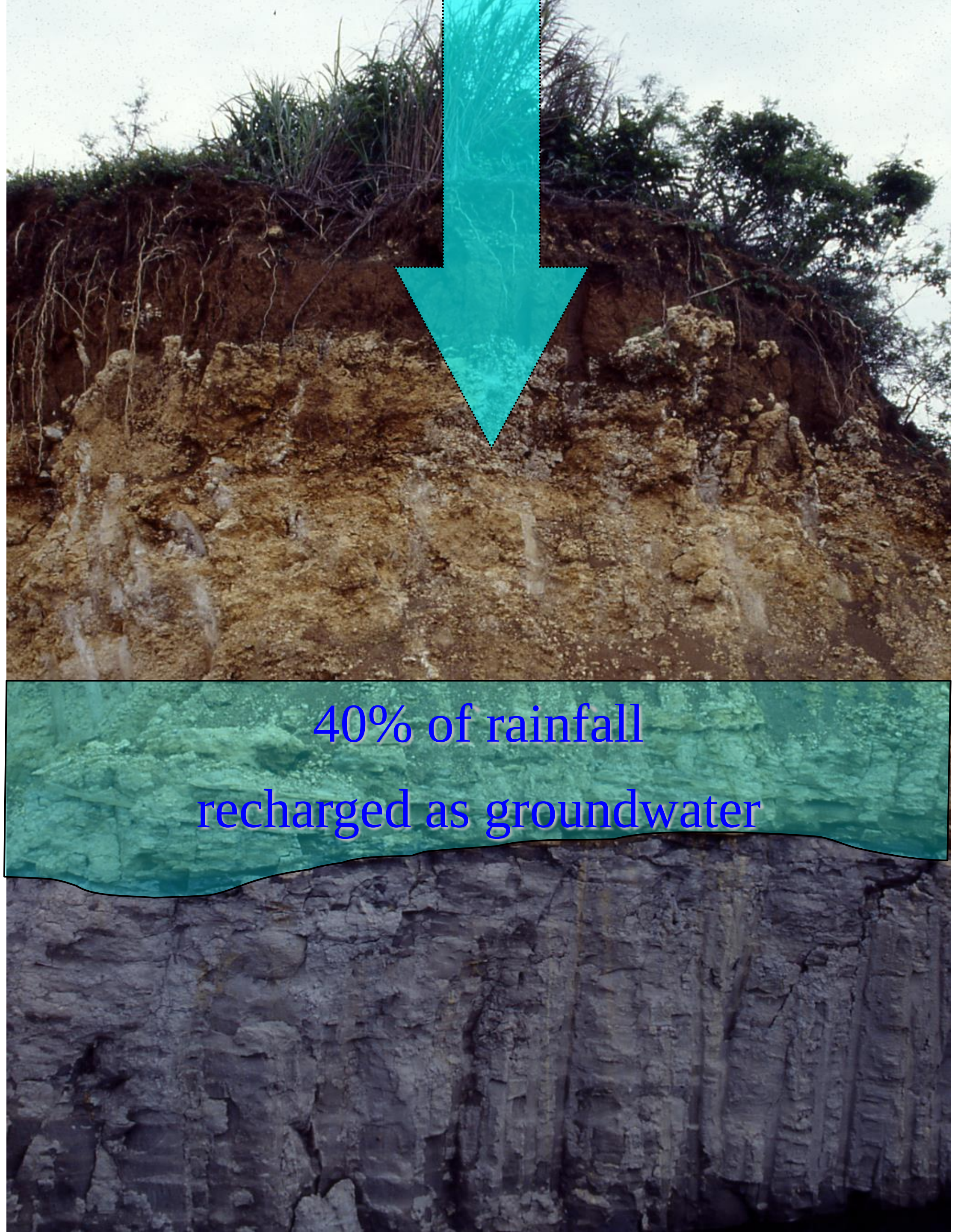
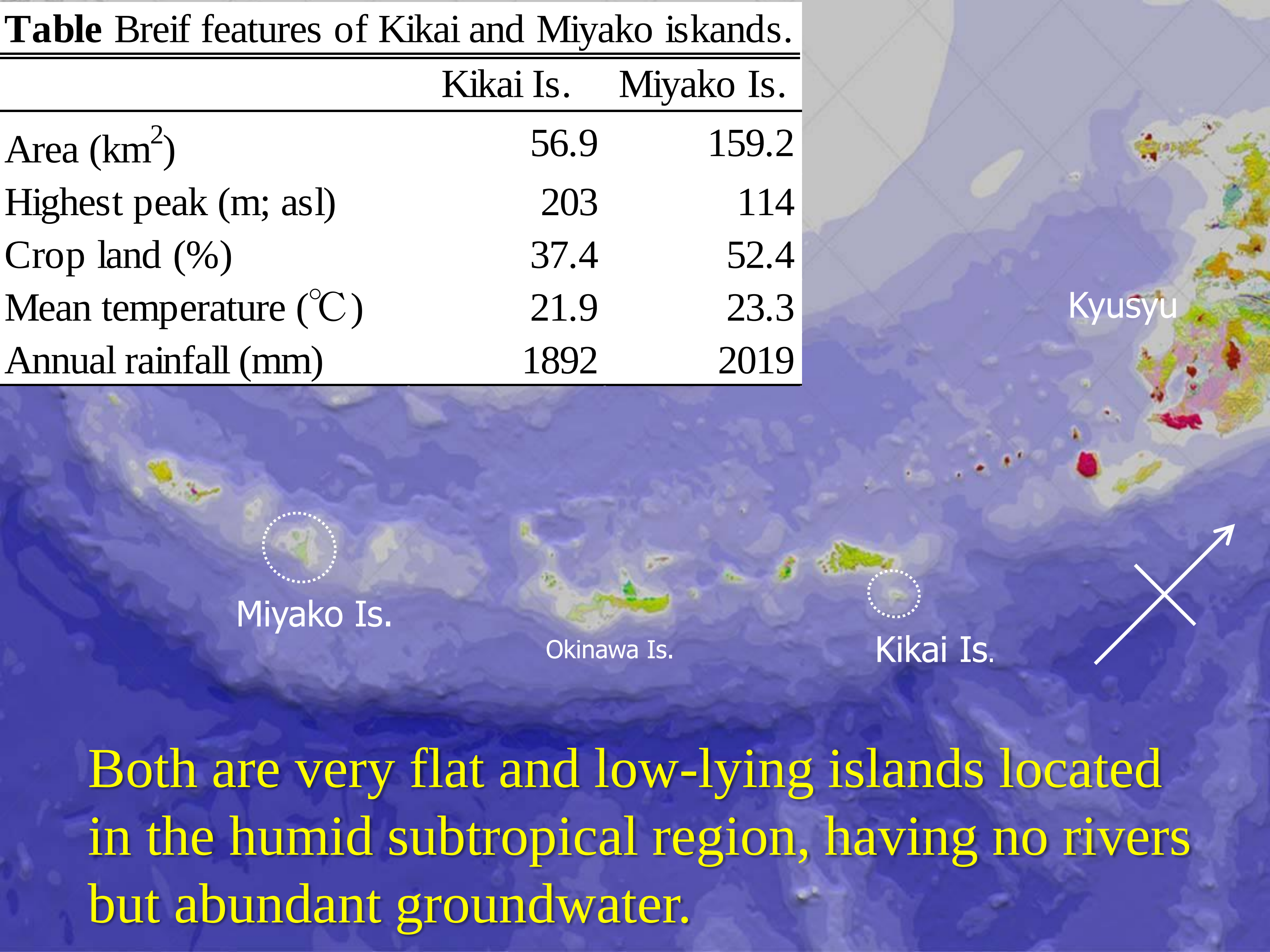


Table Breif features of Kikai and Miyako iskands.

	Kikai Is.	Miyako Is.
Area (km^2)	56.9	159.2
Highest peak (m; asl)	203	114
Crop land (%)	37.4	52.4
Mean temperature (℃)	21.9	23.3
Annual rainfall (mm)	1892	2019



Both are very flat and low-lying islands located in the humid subtropical region, having no rivers but abundant groundwater.

Experiment 1:Inspection in groundwater chemistry

Table Forms of nitrogen in chemical fertilizer and weight % in total nitrogen sold on Kikai Is.

Chemical fertilizer sold on Kikai Is.	Contribution in nitrogen (weight %)
$(NH_4)_2SO_4$	90
$(NH_2)_2CO$	10

Ammonium sulfate was the major fertilizer on Kikai Is. as well as on Miyako Is.

Experiment 1: Inspection in groundwater chemistry Results

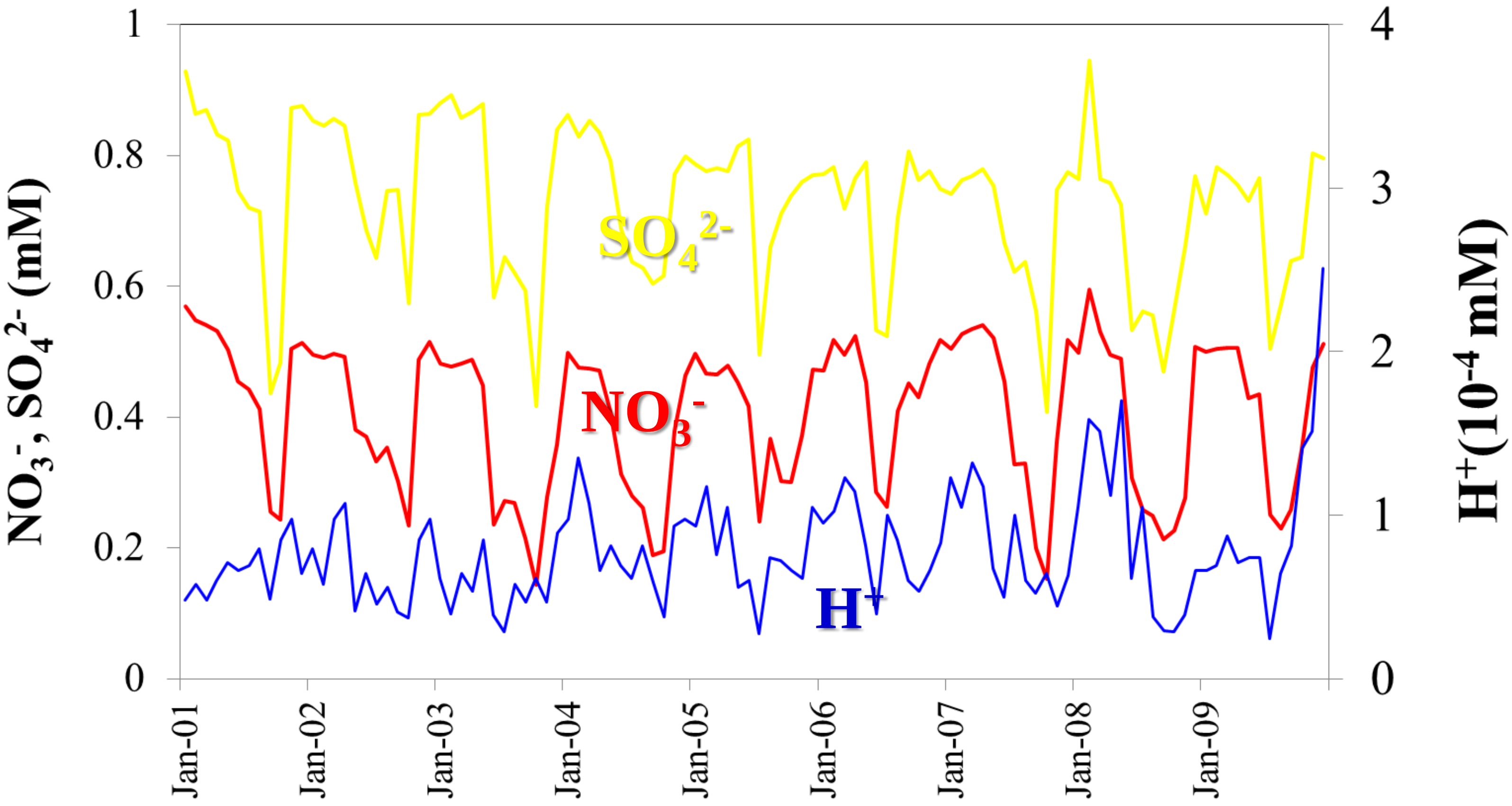


Fig. Changes of concentrations of NO_3^-, SO_4^{2-} and H^+ in groundwater at Point K in agricultural area on Kikai Is.

Change of H^+ concentration in groundwater have synchronized with those of NO_3^- and SO_4^{2-}.

Experiment 1: Inspection in groundwater chemistry Results

Table Difference of hydrogen ion concentration in groundwater between agriculture area and forest area

Land use	Number of monitoring point	H^+ $\times 10^{-4}$ mM
Agriculture	24	0.73
Forest	3	0.46

H^+ concentrations in groundwater were much higher in agriculture area than those in forest area. ⇒ The pH values of groundwater were much lower in agriculture area than those in forest area.

Experiment 1:Inspection in groundwater chemistry Results

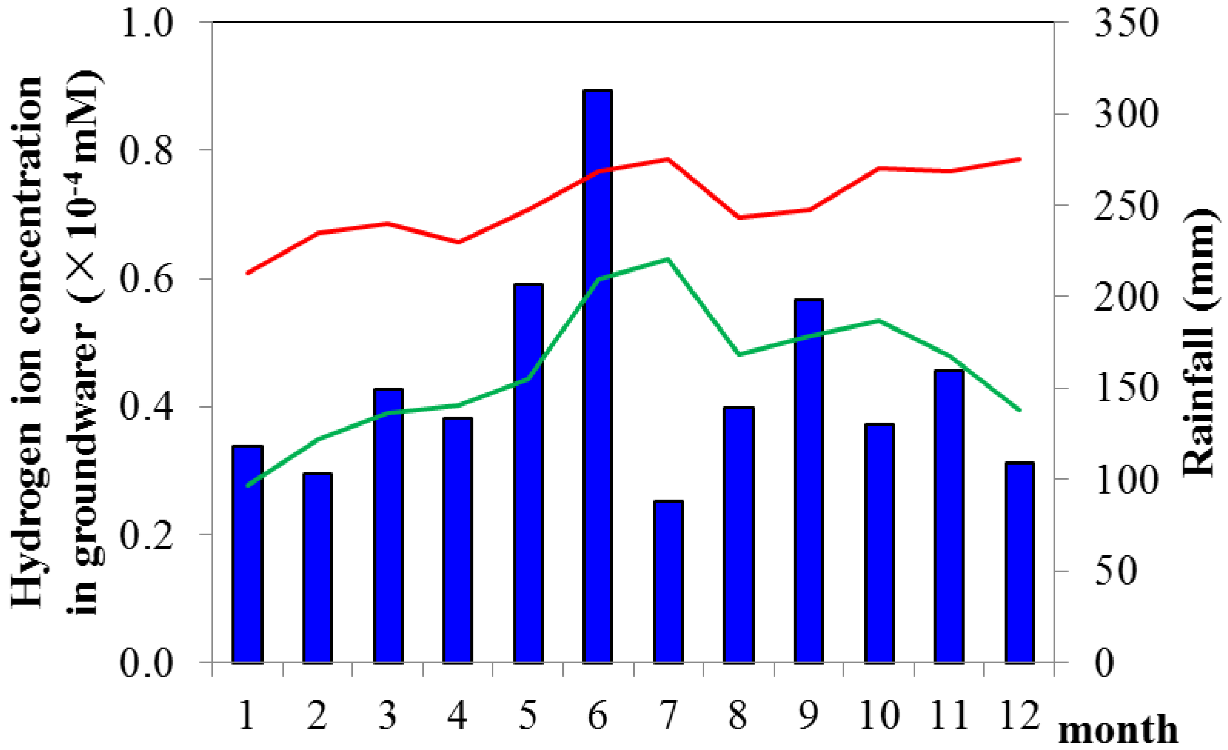


Fig. Difference of monthly mean hydrogen ion concentration in groundwatr between agriculture area and foresr area on Kikai Is.

Differences of H^+ concentration between in agriculture area and forest area were grater in winter, or became greater after chemical fertilizer application started to sugarcane.

Experiment 1:Inspection in groundwater chemistry Results

Table Diffference of (Ca^{2+} + Mg^{2+}) concentration in groundwater between agriculture area and forest area

Land use	n	(Ca^{2+}+Mg^{2+}) mM
Agriculture area	24	2.84
Forest area	3	2.03

The average of (Ca^{2+} + Mg^{2+}) concentration in groundwater was much higher in agriculture area than that in forest area.
⇒ It indicated that carbonates dissolution was promoted in the agriculture area.

Experiment 1:Inspection in groundwater chemistry Results

Table Correlation among NO_3^-, SO_4^{2-}, and $(Ca^{2+} + Mg^{2+})$ concentrations in groundwater

	NO_3^-	SO_4^{2-}
SO_4^{2-}	0.798 **	
$(Ca^{2+} + Mg^{2+})$	0.622 **	0.865 **

**: $P < 0.01$

The assumed origins of NO_3^- and SO_4^{2-} are $(NH_4)_2SO_4$, and of $(Ca^{2+} + Mg^{2+})$ is carbonates.

Experiment 1:Inspection in groundwater chemistry Results

Concentration rate of (Ca^{2+} + Mg^{2+}) in groundwater to that in forest area represents dissolution rate of carbonates in agriculture area to that in forest area.

$$Ca_{(1-x)}Mg_xCO_3 + (NH_4)_2SO_4 + 4O_2 \rightarrow (1-x)Ca^{2+} + xMg^{2+} + 2NO_3^- + SO_4^{2-} + 4H_2O + 2CO_2 \quad \cdots(5)$$

Table Difference of (Ca^{2+} + Mg^{2+}) concentration between agriculture area and forest area

	mM	Relative dissolution rate
Forest area	1.66	1
Agriculture area (ave.)	2.84	1.7
Agriculture area (max.)	3.87	2.3

Experiment 1:Inspection in groundwater chemistry Results: Difference of concentration rate of $HCO_3^-/(Ca^{2+}+Mg^{2+})$ in groundwater

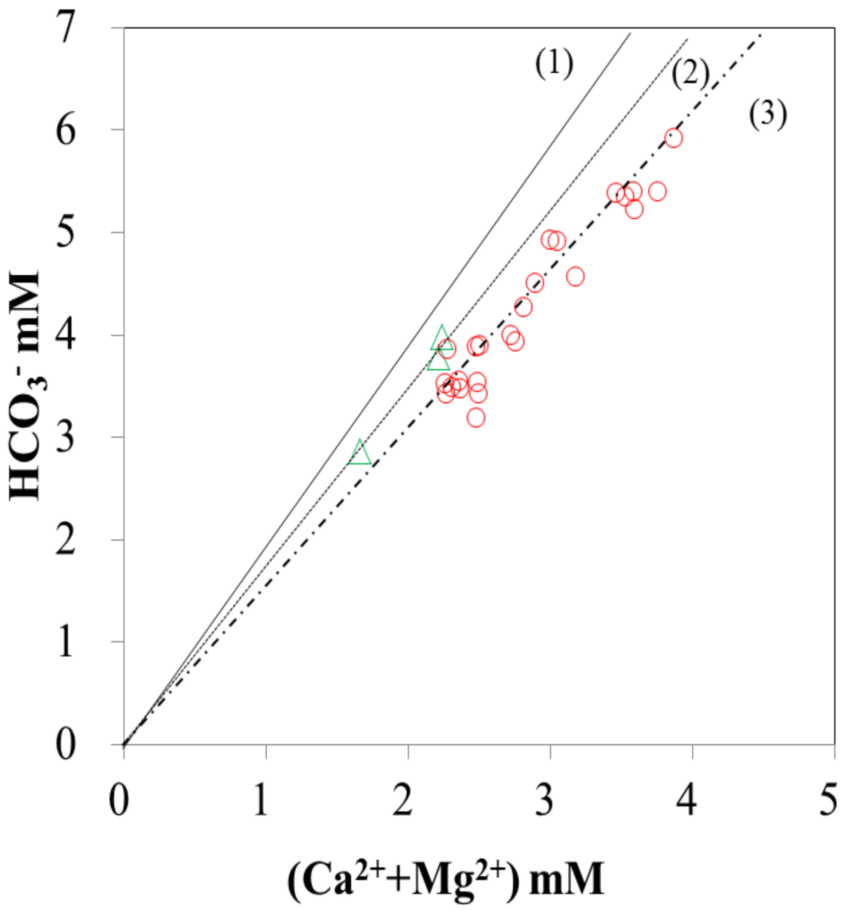


Fig. Relationship between concentrations of HCO_3^- and $(Ca^{2+}+Mg^{2+})$ in groundwater of agriculture area (red circles) and forest area (green circles)

Theoretical formula of carbonates dissolution in natural:

$$\mathbf{Ca_{(1-x)}Mg_xCO_3 + CO_2 + H_2O \rightarrow \underset{1\ \text{mol}}{\underline{(1-x)Ca^{2+} + xMg^{2+}}} + \underset{2\ \text{mol}}{\underline{2HCO_3^-}}}$$

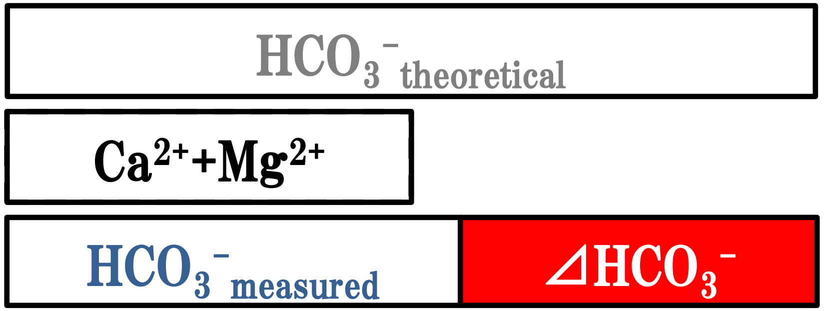
Line (1) Theoretical: y = 2x
Line (2) Forest area: y = 1.74x
Line (3) Agriculture area: y = 1.52x

Concentration ratios of HCO_3^- to $(Ca^{2+}+Mg^{2+})$ in the agriculture area were lower than the theoretical ratios and those in of the forest area.

Experiment 1:Inspection in groundwater chemistry

Results

$\Delta HCO_3^- = HCO_3^-{}_{theretical} - HCO_3^-{}_{measured}$



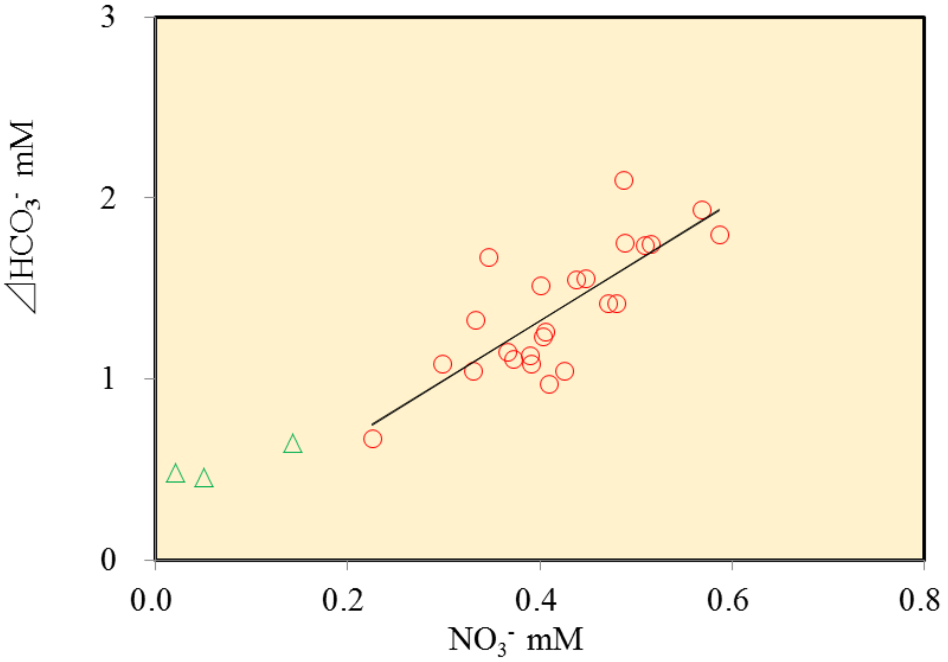


Fig. Relationship of ΔHCO_3^- with NO_3^- in agriculture area (red) and forest area (green)

Experiment 1:Inspection in groundwater chemistry

Results

Table SIc and partial pressure of CO_2 in groundwater of different land use

Land use	SIc	Partial pressure of CO_2 $\log((P\ co_2)/atm)$
Agriculture	0.64	-1.68
Forest	0.58	-1.97
Common air	—	-3.41

SIc: Saturation index of HCO_3^- in groundwater to carbonates dissolution; 0 > unsaturated, 0 = saturated, 0 < oversaturated

In groundwater samples of agriculture area, HCO_3^- concentrations was oversaturated to carbonates dissolution and the partial pressure of CO_2 was higher than that of forest area.

The result indicated that carbon released from carbonates dissolution was emitted in a form of CO_2 at spring mouth, especially in the agriculture area.

Experiment 2:CO_2 monitoring and investigation of actual condition of fertilizer application

① Monitoring of CO_2 concentration at spring mouth and groundwater

Study area: Agriculture and forest area on Miyako Island

Period: Once a week from Mar. 2009 to Mar. 2010 (n = 50)

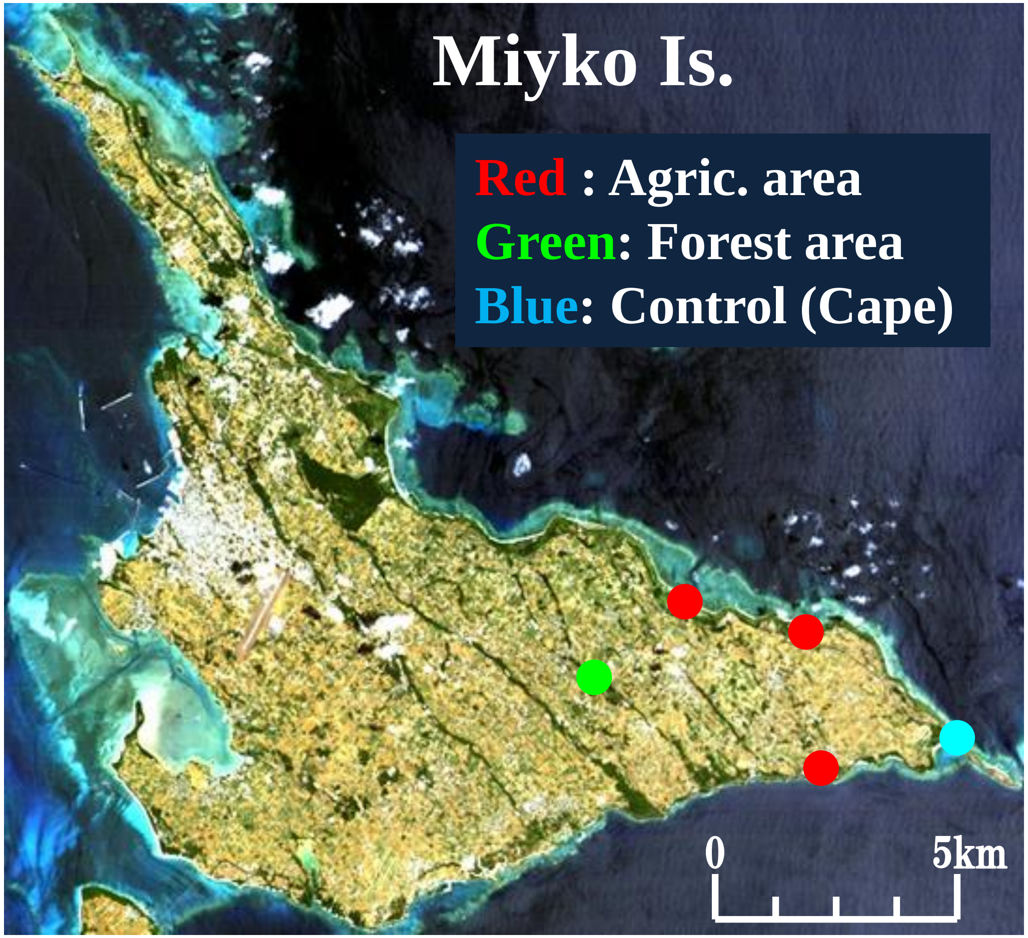
Survey item: H^+, Na^+, NH_4^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, HCO_3^-, Sic, and $P\text{co}_2$

②Application amount of chemical fertilizer

Study area: Miyako Island

Period: From 2009 to

Experiment 2: CO_2 monitoring and investigation of actual condition of fertilizer application




Agric. area 1


Agric. area 2


Agric. area 3


Forest area


Control (Cape)

Monitoring points for CO_2: 3 points in agriculture area, 1 point in forest area, and 1 point for control on a cape.

Monitoring for groundwater component: the same points other than the cape.

Experiment 2: CO_2 monitoring and investigation of actual condition of fertilizer application Result

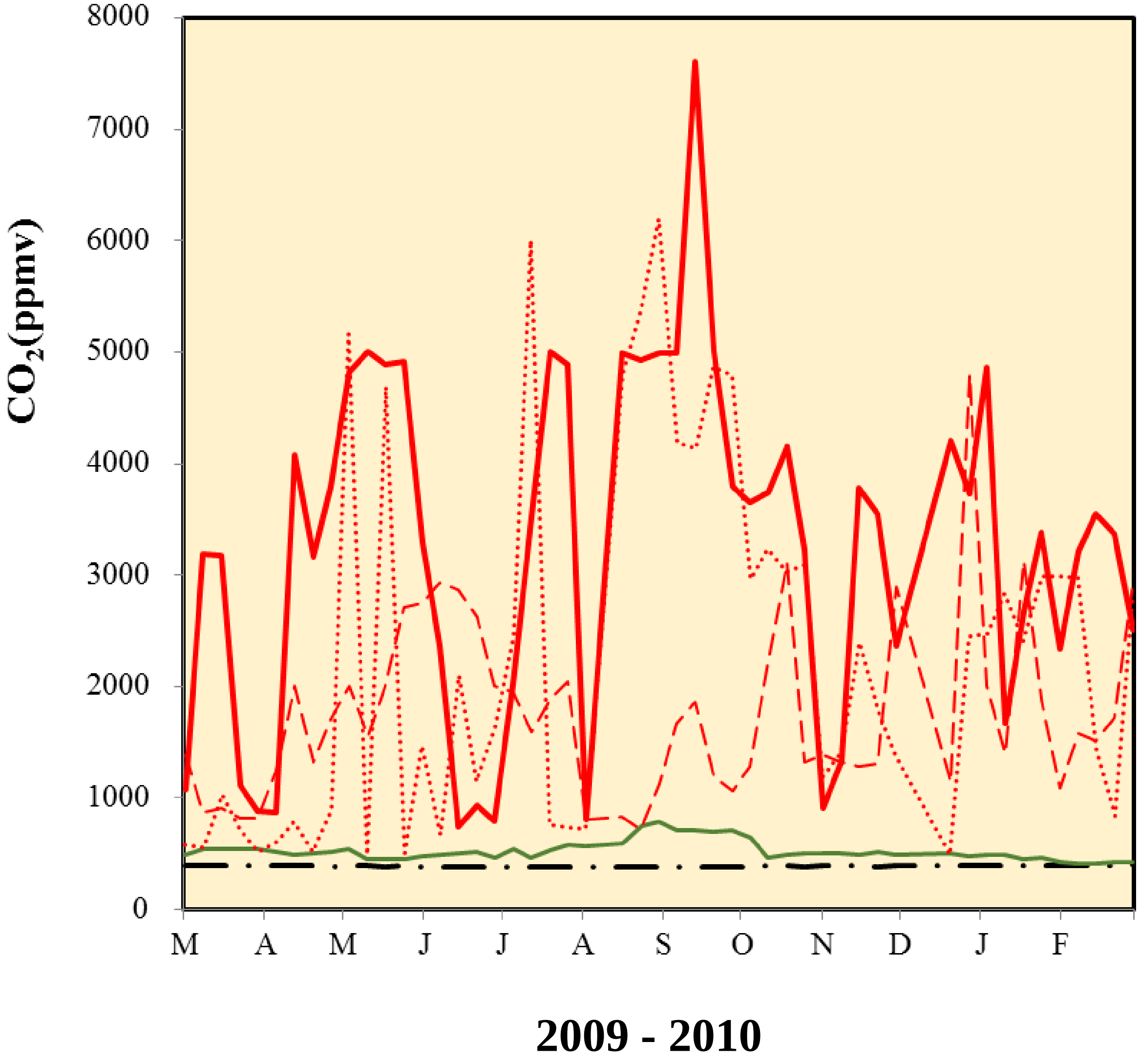


Fig. Changes of CO_2 concentration at spring mouth in agriculture area (red), forest area (green), and common air (black).

Experiment 2:CO_2 monitoring and investigation of actual condition of fertilizer application Result

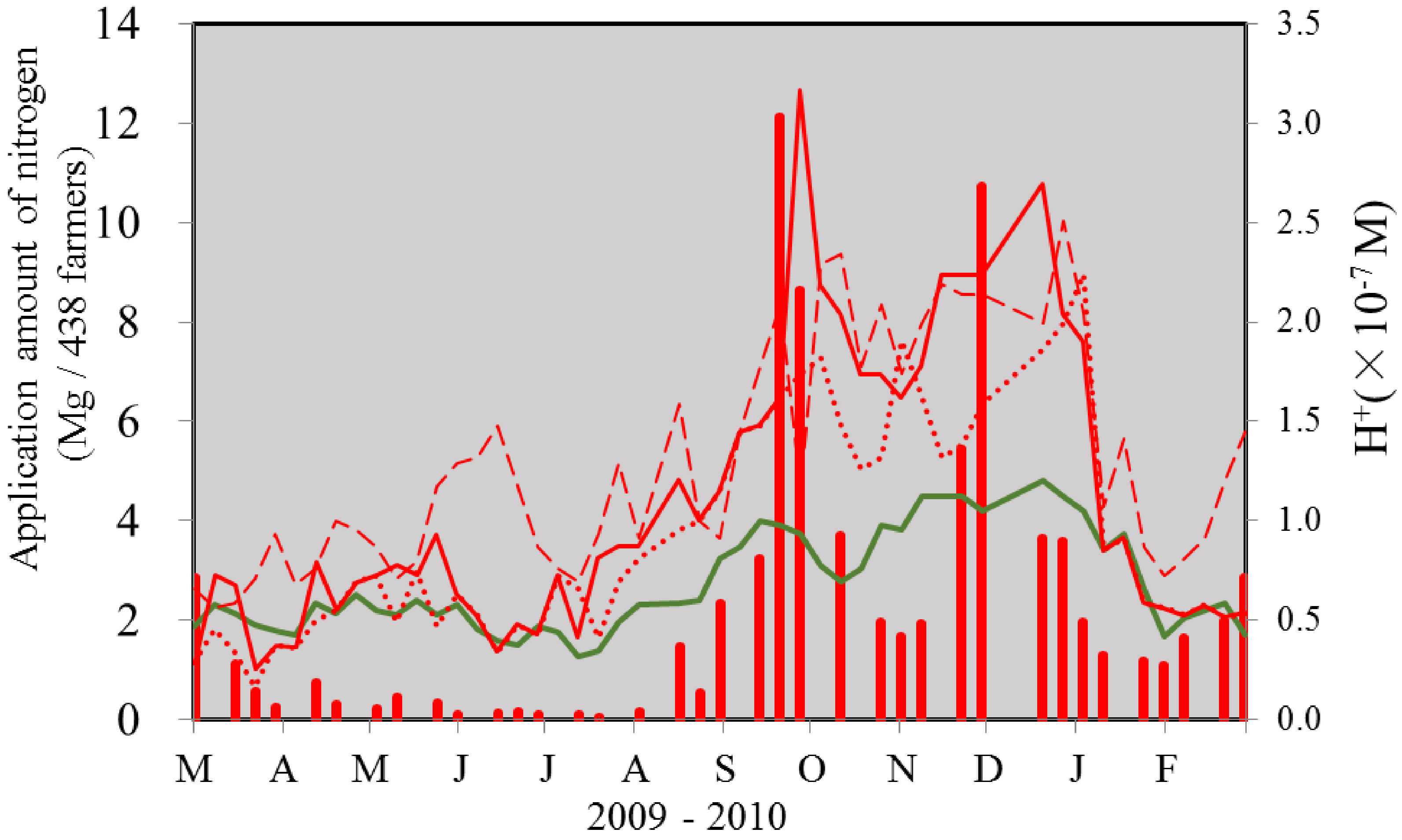


Fig. Relationship of hydrogen ion concentration in groundwater of agriculture area (red) and forest area (green) with application amount of nitrogen

Experiment 2:CO_2 monitoring and investigation of actual condition of fertilizer application Result

	Agriculture area	Forest area
	(n = 3)	(n = 1)
H^+	0.331 *	0.235
Na^+	0.125	0.289 *
K^+	0.023	-0.218
Ca^{2+}	0.480 **	-0.137
Mg^{2+}	0.089	0.038
Cl^-	0.098	0.046
NO_3^-	0.478 **	0.033
SO_4^{2-}	0.266	-0.195
HCO_3^-	0.101	-0.152
⊿HCO_3^-	0.461 **	-0.101
Water temp.	0.466 **	0.537 **
Air temp.	0.150	0.535 **

Table Relationship of CO_2 concentration at spring mouth with groundwater components and temperatures

Experiment 2:CO_2 monitoring and investigation of actual condition of fertilizer application Result

Designing an equation to estimate CO_2 concentration at spring mouth by multiple regression analysis

Agriculture area:

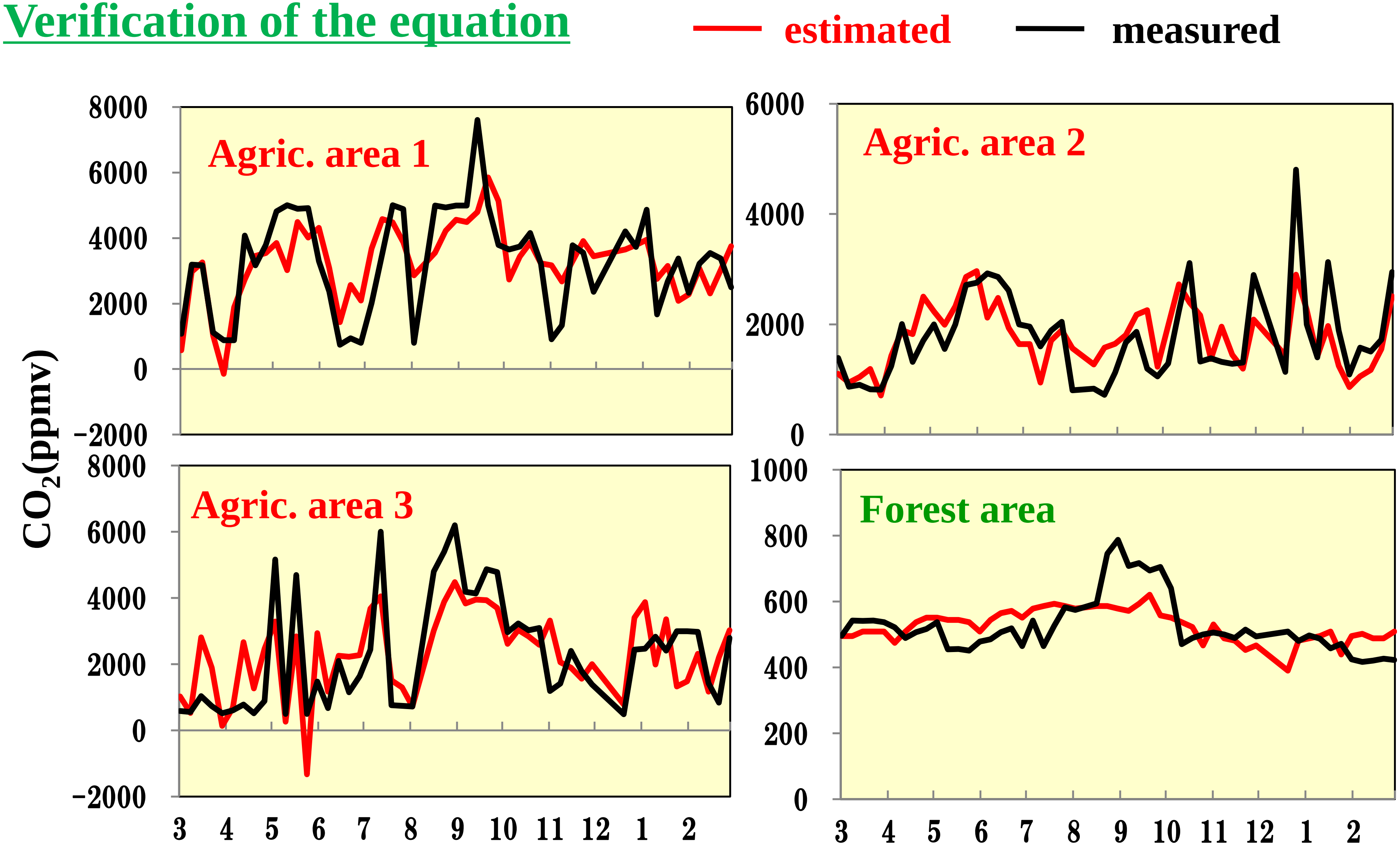
$$CO_2 = a \times (\text{water temp.}) + b \times [H^+] + c \times [Ca^{2+}] + \text{constant}$$

Forest area:

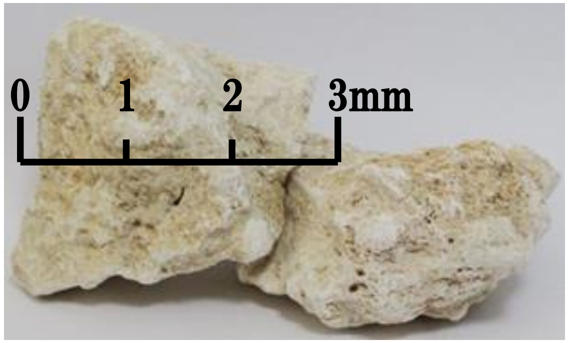
$$CO_2 = a \times (\text{water temp.}) + \text{constant}$$

Experiment 2:CO_2 monitoring and investigation of actual condition of fertilizer application Result

Verification of the equation



Experiment 3: A model study using experimental columns



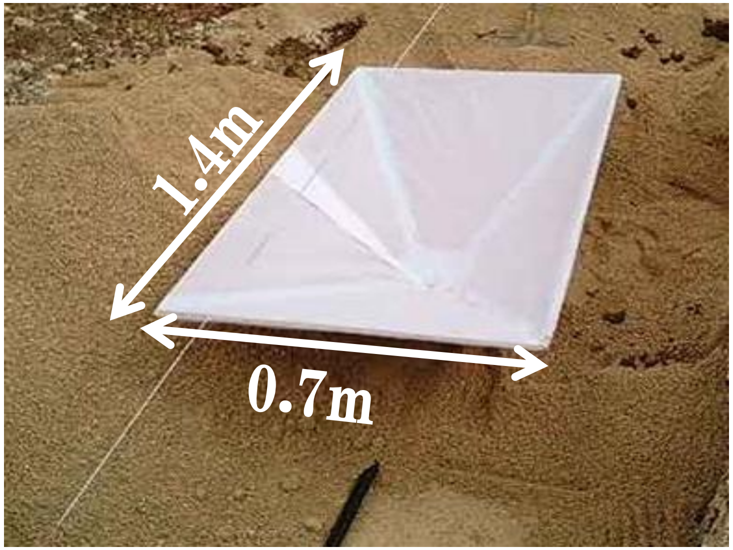
The Ryukyu Limestone filled in the column below

Columns used in the study

Apparatus to collect CO_2 from upward of the column

Collection of percolated water through the column and CO_2 from downward of the column

Experiment 4: Verification in a sugarcane field



Settlement of a lysimeter

Settlement of a lysimeter

Collection of percolated water

Measurement of CO_2 flux from soil

Conclusions

1) Dissolution speed of carbonates in agriculture area was almost double of that in forest area.

2) It was considered that the factors to accelerate the dissolution were the following two;
   - Hydrogen ion produced in soil through nitrification.
   - Decline of neutralizing capacity of soil by negative ions, such as NO_3^- and SO_4^{2-}) derived from chemical fertilizer.

3) Carbon released in the dissolution process is firstly dissolved in groundwater and it emitted as CO_2 when HCO_3^- in groundwater is oversaturated to carbonates dissolution and the groundwater meets air having less partial pressure of CO_2 than that in the water.

Conclusions

4) Most of CO_2 produced in the dissolution move downwards with percolation water.

5) CO_2 concentrations at spring mouth can be shown using the following factors;

Agriculture area: groundwater temperature, H^+ and Ca^{2+} in groundwater

Forest area: groundwater temperature

Conclusions

It is estimated that the total emission amount of carbon is 0.27～0.46 Gt C yr^{-1}, or 3.7～6.4 % in all the anthropogenic emission, when nitrogenous chemical fertilizer is applied in all the carbonates area in the world, with the same manner and the same emission speed as in this case study.

Thus, in order to control the CO_2 emission from the carbonates dissolution,

It is important to choose the fertilizer that is not likely to be nitrified and not acidify soil, and to use the fertilizer efficiently in cropping.

Thank you for your attention !

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