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Formation of Microbial Mats and Salt in Radioactive Paddy Soils in Fukushima, Japan

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Abstract: Coastal areas in Minami-soma City, Fukushima, Japan, were seriously damaged by radioactive contamination from the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident that caused multiple pollution by tsunami and radionuclide exposure, after the Great East Japan Earthquake, on 11 March 2011. Some areas will remain no-go zones because radiation levels remain high. In Minami-soma, only 26 percent of decontamination work had been finished by the end of July in 2015. Here, we report the characterization of microbial mats and salt found on flooded paddy fields at Karasuzaki, Minami-soma City, Fukushima Prefecture, Japan which have been heavily contaminated by radionuclides, especially by Cs (^{134}Cs, ^{137}Cs), ^{40}K, Sr (^{89}Sr, ^{90}Sr), and $^{91 \text{ or } 95}$Zr even though it is more than 30 km north of the FDNPP. We document the mineralogy, the chemistry, and the micro-morphology, using a combination of micro techniques. The microbial mats were found to consist of diatoms with mineralized halite and gypsum by using X-ray diffraction (XRD). Particular elements concentrated in microbial mats were detected using scanning electron microscopy equipped with energy dispersive spectroscopy (SEM-EDS) and X-ray fluorescence (XRF). The objective of this contribution is to illustrate the ability of various diatoms associated with minerals and microorganisms which are capable of absorbing both radionuclides and stable isotopes from polluted paddy soils in extreme conditions. Ge semiconductor analysis of the microbial mats detected ^{134}Cs, ^{137}Cs, and ^{40}K without ^{131}I in 2012 and in 2013. Quantitative analysis associated with the elemental content maps by SEM-EDS indicated the possibility of absorption of radionuclide and stable isotope elements from polluted paddy soils in Fukushima Prefecture. In addition, radionuclides were detected in solar salts made of contaminated sea water collected from the Karasuzaki ocean bath, Minami-soma, Fukushima in 2015, showing high Zr content associated with ^{137}Cs and ^{40}K without ^{131}I. The results obtained here provide evidence of the ability of microorganisms to grow in this salty contaminated environment and to immobilize radionuclides. It is possible that the capability of radioactive immobilization can be used to counteract the disastrous effects of radionuclide-polluted paddy soils.

Keywords: the Great East Japan Earthquake; tsunami; FDNPP accident; radionuclide; paddy soils; microbial mats; solar salt; XRD; XRF; SEM-EDS; Ge semiconductor; diatom; microorganisms; gypsum; halite; Zr content

1. Introduction

Coastal areas in Minami-soma City, Fukushima, Japan, were seriously damaged by the radioactive contamination from Fukushima Daiichi Nuclear Power Plant (FDNPP) accident that caused multiple pollution by tsunami and radionuclide exposure, after the Great East Japan Earthquake, on 11 March 2011 (Figure 1). Four and half years after the events started unfolding at Fukushima No.1, the Japanese government, the nuclear utilities and the Nuclear Regulation Authority (NRA) have not succeeded in overcoming complete planning insecurity of investors. Decontamination workers have cleaned up a contaminated residential area in the city of Minami-soma, Fukushima Prefecture. Families have obtained permission to stay for three months now that radiation levels are low. Fukushima evacuees have returned home. On the other hand, some areas will remain no-go zones because radiation levels remain high. In Minami-soma, only 26 percent of decontamination work had been finished by the end of July in 2015. However, natural falls in radiation levels were taken into consideration [1].

There are various radionuclides not only in the atmosphere, but also in seawater, such as ^{35}S, ^{7}Be, ^{10}Be, and ^{22}Na which have their origin in cosmic rays, ^{222}Rn, ^{210}Pb (^{210}Po), ^{40}K, U, and Th isotopes which have their origin in the land, and ^{90}Sr, ^{137}Cs, ^{239,240}Pu *etc.* which have their origin in atmospheric nuclear tests and/or mainly the FDNNP accident in 2011. FDNPP leaked 17 kinds of radionuclides, such as ^{134}Cs (1.8×10^{16} Bq; half-life 2.1 years), ^{137}Cs (1.5×10^{16} Bq; half-life 30.0 years), ^{90}Sr (1.4×10^{14} Bq; half-life 29.1 years), and ^{95}Zr (1.7×10^{13} Bq; half-life 64.0 days) to the atmosphere and seawater in Japan [2]. The paddy soils at Karasuzaki, Minami-soma City in Fukushima Prefecture were heavily contaminated by radionuclides, especially by Cs (^{134}Cs, ^{137}Cs) and Sr (^{89}Sr, ^{90}Sr), even though it is more than 30 km north of the FDNPP (Figure 2).

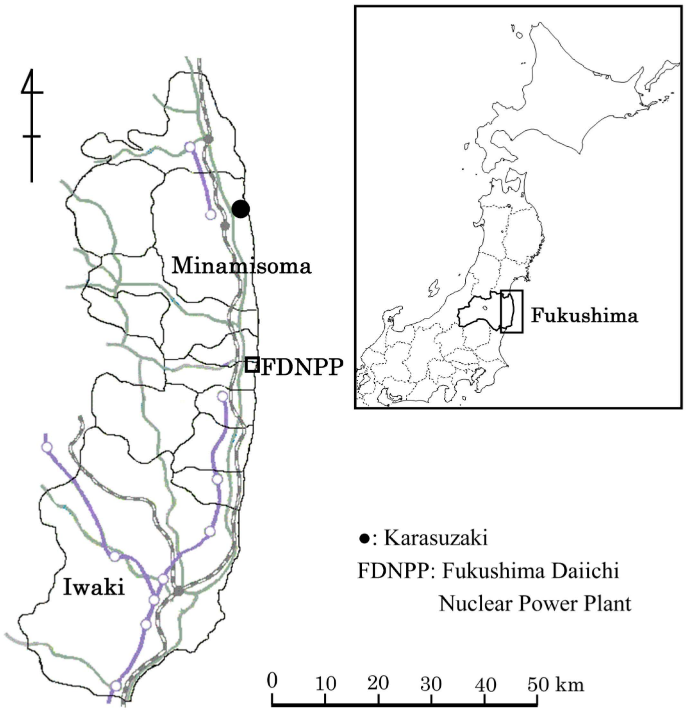

Figure 1. Location map shows an outcrop of the microbial mats (●) after the tsunami and FDNPP accident, in Karasuzaki, Minami-soma City, Fukushima Prefecture, Japan.

The characteristics of the microbial mats formed after 2011 off the Pacific coast of the Tohoku Earthquake (henceforth the 3.11 Earthquake) were clarified by studies of their living environment, chemical compositions, and microscopic observations at Minami-soma City, Fukushima Prefecture, Japan which was itself damaged by salt water of the tsunami after the 3.11 Earthquake [3,4].

Few studies and little direct experimental evidence are available on microbe-radionuclide-salt interactions in paddy soils. In this study analyses were carried out on radionuclide-bearing micro-organisms, revealing biomineralization of nanometer scale in the context of radioactive environmental remediation.

The objective of this paper is to introduce the ability of various diatoms associated with minerals and salt capable of absorbing both radionuclides and stable isotopes from polluted paddy soils in Minami-soma City, Fukushima, Japan, which were damaged by sea water of the tsunami after the 3.11 Earthquake.

Here, we report the characterization of microorganisms with minerals and salt observed on the surface of a paddy field in Karasuzaki, Fukushima., The use of advanced analytical techniques including X-ray diffraction (XRD), scanning electron microscopy equipped with energy dispersive spectrometer (SEM-EDS), X-ray fluorescence analysis (XRF) and Ge semiconductor analysis enable the documention of micron and sub micrometer-scale chemical and structural features, and identification of dose rate and radionuclides in microbial mats. In addition, the comparison with solar salts from sea water allows discussion of the radioactive elements and effects of such objects during the formation of microbial mats.

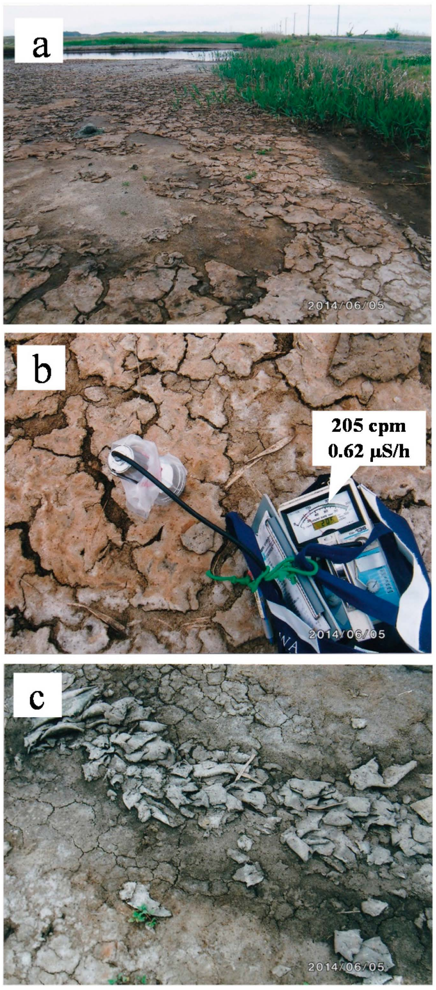

Figure 2. Views of paddy soils, showing microbial mats on the tsunami sediments (**a**); network of "healed" cracks, overgrown by radioactive microbial mats, forming bulges spanning the cracks (**b**); and dried white microbial mats rich in salts (**c**).

2. Materials and Methods

2.1. Investigated Specimens

The investigated microbial mats were collected on the flooded paddy fields near Karasuzaki fishing port (37°40.797′; 141°00.223′), Kashima, Minami-soma City, Fukushima Prefecture, Japan which were damaged by seawater of the tsunami and FDNPP accident after the 3.11 Earthquake. White and brown microbial mats, several mm in thickness, formed on the surface of the flooded paddy fields. The paddy soil temperature was 32.7 °C, pH 8.1, electric conductivity (EC) > 200 mS/m, oxidation-reduction potential (ORP) 58 mV (in the field), ORP 259 mV (at 25 °C), salinity 27‰, dose rate 0.59 μSv/h (in the air) and 0.62 μSv/h (in the sediments), on 15 September 2012. The white-light brown in color microbial mats on the surface of the paddy fields were dried up. The white microbial mats on the top of the surface in the paddy fields and black sandy sediments of paddy soils, underneath the microbial mats, were collected for this study, on the 15 September 2012. At that time, the air dose rate was 0.27–0.59 μSv/h, microbial mats were 0.59–0.65 μSv/h, and paddy soils and sediments were 0.35–0.62 μSv/h. The reverse side of the microbial mats indicated a lower dose rate of 0.48 μSv/h.

The microbial mats have developed to become thicker and thicker year by year. The thickness of the microbial mats was several mm on 5 June 2014. The dose rate of the surface was still high at 205 cpm (0.62 μSv/h). The surface of the white microbial mats became dried out during the summer, giving cracks rich in salts on the top of the surface.

Radioactively contaminated sea water was collected from Karasuzaki ocean bath, Minami-soma City, Fukushima, salts were made by boiling and sunbaking (solar) salts in April, May, and June, 2015. The leak of radioactive ^{134}Cs, ^{137}Cs, ^{40}K, ^{90}Sr and traces of some radionuclides originated from the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident. However, the concentrations of radionuclides in seawater were at the level of 1–3 mBq· L^{-1} and, without using several hundred liters of seawater, it is difficult to measure radium isotopes with precision for the analyses of circulation of seawater. In this paper, we would like to introduce the results obtained for radionuclides in solar salts made from coastal seawater in Minami-soma City, Fukushima.

2.2. X-Ray Diffraction

X-ray powder diffract meter (XRD) (Rinto 2200, Rigaku, Tokyo, Japan; Cu-Kα radiation, 40 kV, 30 mA, scan speed of 2°/min) was used for identification of minerals in paddy field sediments and microbial mats in Karasuzaki, Minami-soma City, Fukushima, Japan. The clay fractions of <2 μm size were oriented on a glass slide.

2.3. ED-XRF Chemical Analyses

Chemical compositions (wt %) of the paddy soils and microbial mats were determined by energy dispersive X-ray fluorescence analyzer (ED-XRF) of JSX-3201 and XRF-JSX-3100RII (JEOL, Tokyo, Japan), using a Rh-Kα ray instrument, which operated at an accelerating voltage of 30 kV, under vacuum condition, and FP bulk qualitative and quantitative analyses.

2.4. Ge Semiconductor Analysis

Car-borne and hand-borne radiation measurement systems were used in the field in Karasuzaki, Minami-soma City, Fukushima. Measurements of β (γ)-ray radiation used an Aloka-GM survey meter TGS-136 (Hitachi-Aloka, Tokyo, Japan) (cpm) and TCS-151 (Hitchi-Aloka) (μSv/h). The radionuclides of microbial mats and solar salts were determined in the laboratory by Ge semiconductor (GC2520, CANBERRA, EnergySolutions Services, Inc. Salt Lake City, UT, USA) and NAI (TI) (CAN-OSP-NAI, Hitachi-Aloka medical, Toyo, Japan), and the instruments detected ^{131}I, ^{40}K, and Cs (^{134}Cs and ^{137}Cs) (Bq/Kg-dry).

2.5. Scanning Electron Microscopy (SEM) Equipped with Energy Dispersive Spectroscopy (EDS)

Scanning electron microscopes (SEM) equipped with energy dispersive X-ray analyzer (EDS) technique (SEM-EDS) can be used to study the microbial mats and solar salts which collected from Karasuzaki, Minami-soma City, Fukushima Prefecture. Here we attempted SEM-EDS observations and semi-quantitative analyses of both radionuclide and stable isotopes.

A scanning electron microscope (S-3400N, Hitachi) equipped with energy dispersive analyzer (Horiba, Kyoto, Japan) (SEM-EDS) was used for morphological observations, semi-quantitative analyses, and elemental content maps, under 15 kV accelerating voltage, current 70–80 μA, with an analytical time of 1000 s, and an area of 10 mm × 10 mm on the carbon double tape with Pt coating.

Note that Zr can be found in sea sand and/or river sand, but not always in all sand grains. Therefore, using XRF we quickly recognized that Zr was present in the sand grains whereas SEM-EDS mapping identified Zr in each specific grain. By taking XRF (wt %) together with SEM-EDS (mass%) we can then extract Zr from the grain mass [5].

3. Results

3.1. Mineralogy of the Microbial Mats

The mineralogy of the microbial mats on the paddy field after the tsunami and FDNPP accident in Karasuzaki, Minami-soma City, Fukushima, as determined using XRD analysis, contains both minerals and amorphous materials (Figure 3). The surface of microbial mats (Figure 3a) indicated that the amorphous background is located at 4 Å [6,7]. The microbial mats were composed of minerals, such as halite (2.82, 1.99, and 1.63 Å), gypsum (7.63, 4.28, 3.07, 2.87 and 2.68 Å) and quartz (3.34 Å).

On the other hand, the reverse side of the microbial mats (Figure 3b) containing mainly minerals in the sandy paddy field, indicated quartz (4.26, 3.34, and 1.82 Å), feldspars (3.35 and 3.18 Å), and halite (2.82 and 1.99 Å) associated with trace of 7 Å clay minerals without high background.

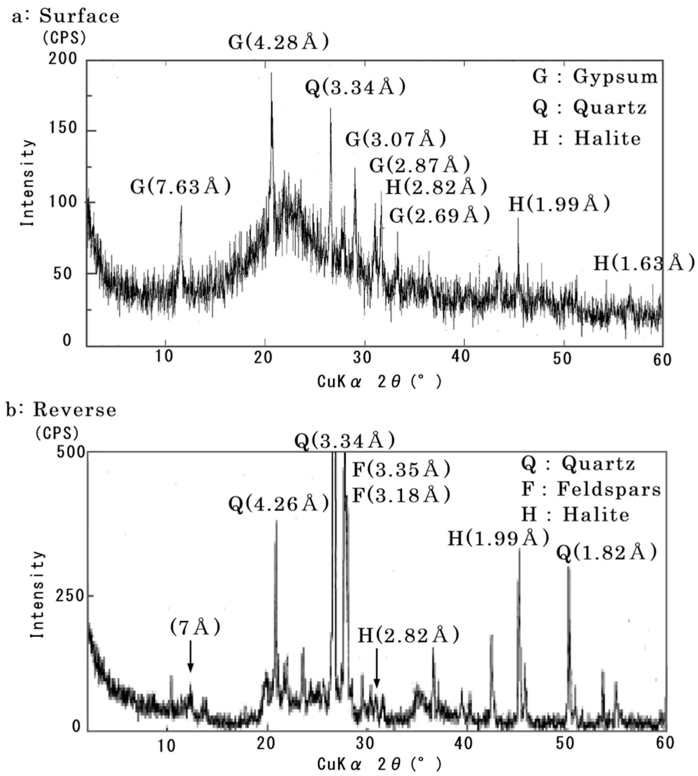

Figure 3. X-ray powder diffraction patterns of the surface (**a**) and the reverse (**b**) of microbial mats collected from Karasuzaki, Minami-soma City, Fukushima Prefecture, Japan.

3.2. Chemical Composition of the Microbial Mats

The chemical composition of microbial mat samples (Table 1) collected from six points on the paddy field after the tsunami and FDNPP accident in Karasuzaki, Minami-soma City, Fukushima, clearly showed the major and trace elements by ED-XRF analyses (Table 1). The elements of Na, Mg, Al, Si, Cl, K, Ca, and Fe are major elements, associated with trace elements of P, Ti, and Mn which are attributed to sea water and sea sand carried by the tsunami. The traces of Cr, Ni, Cu, Zn, Br, Rb, Sr, Zr, and Ba can be ascribed to both the tsunami and FDNNP accidents, SEM-EDS semi-quantitative analyses shown in Table 3.

Table 1. X-ray fluorescence (XRF) analyses of microbial mats on the surface of paddy soils in Karasuzaki, Minami-soma City, Fukushima Prefecture, Japan. Analyzed on 4 June 2013 (wt %).

Element	Samples					
	No.1	**No.2**	**No.3**	**No.4**	**No.5**	**No.6**
Na	2.64	2.57	2.39	2.44	2.31	2.41
Mg	3.52	3.51	2.44	2.19	2.76	2.66
Al	15.5	14.9	16.9	17.7	17.4	17
Si	33.5	32	35.7	42.8	37.2	34.9
P	0.721	0.676	0.421	0.35	0.467	0.417
S	1.76	1.79	1.64	0.931	1.98	1.95
Cl	5.91	6.85	6.38	4.45	5.08	5.89
K	2.12	2.26	2.54	2.96	2.65	2.73
Ca	3.56	4.26	2.66	4.39	3.8	2.65
Ti	0.767	0.881	1.08	2.65	1.63	1.23
Mn	0.842	0.653	0.279	0.337	0.439	0.344
Fe	8.87	10.1	11.3	13.2	14.3	13.1
Cr	0.0233	0.0255	0.0313	0.068	0.0422	0.0331
Ni	0.0117	0.0135	0.0174	0.0159	0.0215	0.0203
Cu	0.0149	N.D.	0.0192	0.0138	0.0243	0.0198
Zn	0.0416	0.0461	0.0461	0.0423	0.0597	0.0609
Br	0.0508	0.0588	0.0492	0.0177	0.0453	0.0533
Rb	0.0166	0.0176	0.0186	0.0148	0.0223	0.0232
Sr	0.048	0.0545	0.0449	0.0522	0.059	0.0571
Zr	N.D.	N.D.	0.043	0.0906	N.D.	N.D.
Ba	0.0335	0.039	0.0524	0.0609	0.0513	0.0559
Total	79.9504	80.705	83.9997	94.7742	90.3416	85.6046
Heated at 600 °C	20.1	19.3	15.9	5.2	9.6	14.4

N.D.: Not Detected

3.3. Radionuclides in the Microbial Mats and Solar Salts (Table 2)

Ge semiconductor analyses of microbial mats at Karasuzaki, Minami-soma City, Fukushima detected abnormally high radiation of ^{134}Cs (1900–2600 Bq/Kg-dry), ^{137}Cs (4000–6000 Bq/Kg-dry) and traces of ^{40}K (370–460 Bq/Kg) on the 5th of June 2013. The isotope ^{131}I was not detected in microbial mats, because the half-life time of ^{131}I is 8.04 days (Table 2). The ratio of ^{134}Cs/^{137}Cs of microbial mats was 0.43–0.52 2 years after the FDNPP accident, because the half-life time for ^{134}Cs is 2.1 years.

On the other hand the ratio of ^{134}Cs/^{137}Cs of paddy soils was 0.7 on the 3 July in 2012, showing a quite high ratio because it was only one year after the FDNPP accident. The microbial mats 2–3 mm thick subsequently developed high radiation levels of 0.62–1.1 μSv/h after 1–2 years, indicating discernible concentrations of radionuclides of actinides (Th, U, and Np) (Table 3). The microbial mats absorb both radionuclides and stable isotope elements from the contaminated paddy soils which is one of the first reports of actual analysis of the natural microbial mats.

Ge semiconductor analyses of the solar salts made of sea water in Karasuzaki ocean bath, Minami-soma City, Fukushima, detected a low ratio of $^{134}Cs/^{137}Cs$ on the 22 April, 14 May, and 6 July in 2015, between 0.08–0.24, four years after the FDNPP accident.

Table 2. Ge semiconductor analysis of microbial mats in 2013, the paddy soils in 2012 (upper), and solar salts in 2015 (lower), in Karasuzaki, Minami-soma City, Fukushima Prefecture, Japan. (Bq/kg-dry).

Radionuclide	Microbial Mats						Paddy Soils
	No.1	No.2	No.3	No.4	No.5	No.6	No.7
^{131}I	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
^{40}K	N.D.	460	N.D.	370	N.D.	N.D.	N.D.
^{134}Cs	2200	2000	2500	1900	2300	2600	19,000
^{137}Cs	4200	4300	5500	4000	4700	6000	27,000
$^{134}Cs/^{137}Cs$	0.52	0.47	0.45	0.48	0.49	0.43	0.7
Hydrate (%)	26.3	25.5	25	7	39.9	39.6	16.8
Analyzed date	5 June 2013						3 July 2012

Radionuclide in Solar Salts	Dose Rate		
^{131}I	N.D.	N.D.	N.D.
^{40}K	369	304.2	344.35
^{134}Cs	4.75	25.3	2.3
^{137}Cs	31.77	106.25	28.3
$^{134}Cs/^{137}Cs$	0.15	0.24	0.08
Analyzed date	22 April 2015	14 May 2015	7 June 2015

N.D.: Not Detected.

3.4. SEM-EDS Analysis of Microbial Mats and Solar Salt

SEM-EDS semi-quantitative analyses of five points in microbial mats and a solar salt collected from Karasuzaki, Minami-soma City, Fukushima, showed particular elements concentrated in each point (Table 3). Related elemental maps for the 1, 2, and 4 points and the solar salt indicated non-uniform distribution of elements within 30 micron-sized areas of diatom, coccus typed bacteria, salt, and clays (Figure 4a,b,c,d). The longer half-life time radionuclides, such as actinides (Th 2%, U 0%–0.17%, Np 1%) were found (Table 3). A trace of Np is present in natural systems whereas the U changes ($^{235}U \geqslant {}^{207}Pb$) by nuclear fission.

SEM-EDS semi-quantitative analyses use the standard Th M (ThO_2), U M (UO_3) and Np M (Np_2O_5), but the Np is not defined. We need another analytical method for cross checking in detail the actinides in the microbial mats.

All maps show abundant Si content (17%–28%), resulting from diatoms, associated with salt grains rich in Na and Cl ascribed to sea water due to the tsunami. Many clay mineral parts contain significant amount of Mg (Figure 4b). The gypsum small grain can be seen in Figure 4b (an arrow). The diatoms are associated with high Si, Sr and Zr signals. However the Al signal is less obvious. The halite (Na and Cl) and gypsum ($CaSO_4 \cdot 2H_2O$) may be attributed to sea water. Abundant coccus typed bacteria were stuck on the surface of diatom cells, identified as the genus *Nitzschia filiformis* and *scalpeliformis* species and were widely distributed (Figure 4). Analytical point 1 contains diatom, coccus typed bacteria and salt, shown in Figure 4a, analytical points 2 and 4 contain diatom, clays, gypsum and salt, shown in Figures 4b,c, respectively.

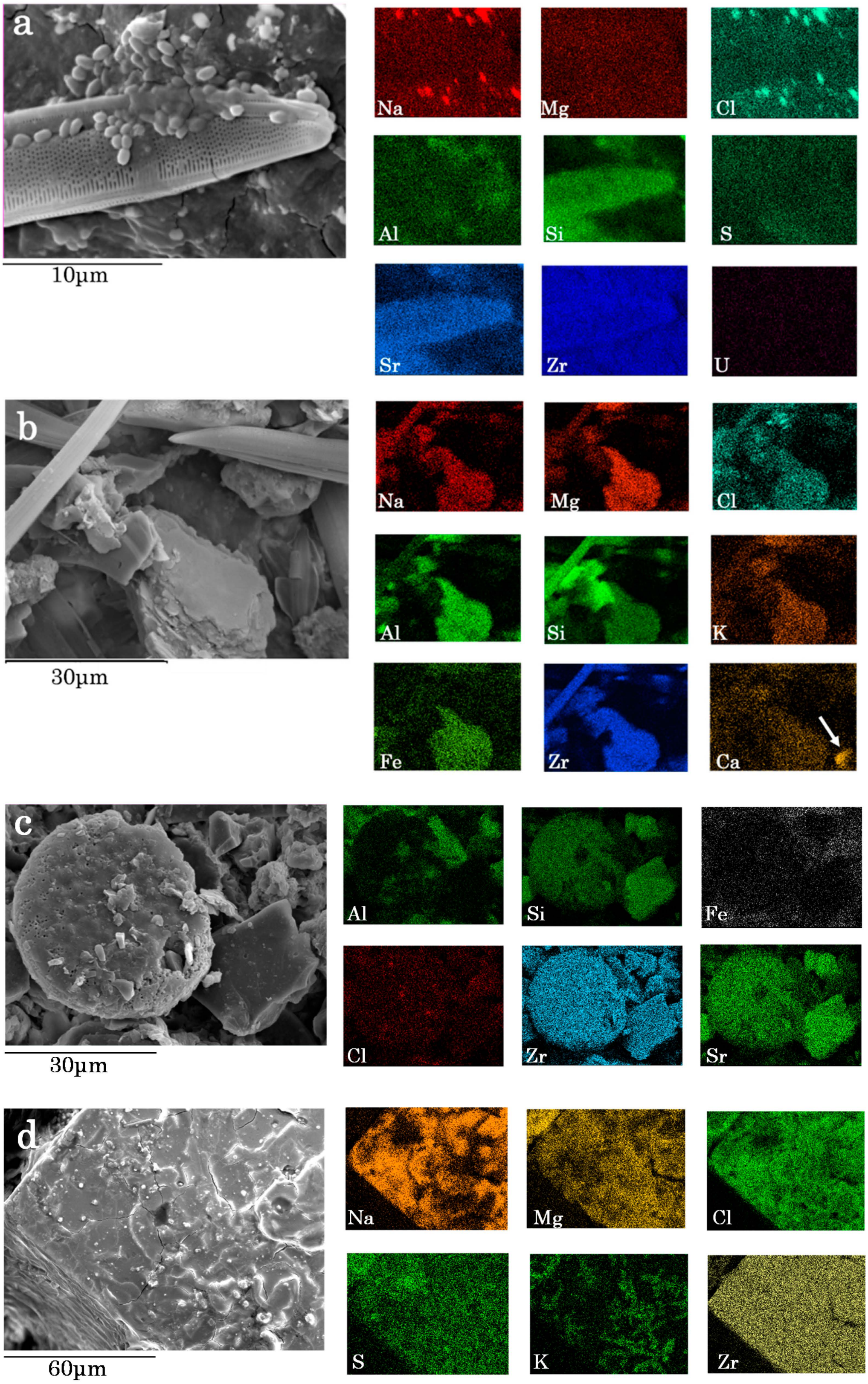

Figure 4. Scanning electron microscopic images and the elemental content maps of microbial mats. Diatom with coccus typed bacteria (**a**), diatom with clays and gypsum (an arrow) (**b**), diatom covered with thick clays (**c**), and solar salts made of sea water (**d**).

Table 3. Energy dispersive spectroscopy (SEM-EDS) semi-quantitative analyses of microbial mats in 2013 and solar salt (Figure 4) in Karasuzaki, Minami-soma City, Fukushima Prefecture, Japan. The analytical points 1, 2, 4, and salt are shown in Figure 4a,b,c,d, respectively. Analyzed on 10 June 2013. (mass%, $\pm$ 3σ).

Elements and Spectrum		Microbial Mats Analytical Point					Solar Salt
		Point 1	Point 2	Point 3	Point 4	Point 5	23 June 2015
Mg	$K\alpha_1$	3.03	2.12	2.06	1.65	2.66	4.71
Al	$K\alpha_1$	1.28	6.1	3.13	6.66	7.49	0
Si	$K\alpha_1$	19.45	26.62	28.08	27.27	17.19	0
S	$K\alpha_1$	2.95	0.51	2.02	0.81	0.35	1.71
Cl	$K\alpha_1$	9.05	2.32	6.58	3.58	6.95	14.53
K	$K\alpha_1$	0.47	1.59	0.56	1.14	1.98	0.86
Ca	$K\alpha_1$	1.57	0.7	1.13	1.15	0.7	0.07
Mn	$K\alpha_1$	0	0.15	0.13	0.12	0.14	0
Fe	$K\alpha_1$	2	11.16	2.73	5.92	11.01	0
Ni	$K\alpha_1$	#	#	#	#	#	0.02
As	$K\alpha_1$	#	#	#	#	#	0.02
Zr	$K\alpha_1$	#	#	#	#	#	4.33
Sn	$K\alpha_1$	#	#	#	#	#	0.02
Zn	$L\alpha_1$	9.97	2.04	7.31	4.67	9.58	#
I	$L\alpha_1$	0.19	0.18	0.08	0.13	0.23	0
Cs	$L\alpha_1$	0	0	0	0.14	0.33	0.01
Ba	$L\alpha_1$	0.23	0.92	0	0.76	2.37	0.01
Nd	$L\alpha_1$	0	0.12	0.13	0.1	0.09	#
Th	$M\alpha$	2.05	1.63	2.05	1.63	2.1	#
U	$M\alpha$	0.15	0.02	0.17	0.14	0	#
Np	$M\alpha$	0.93	1.01	1	0.78	1.26	#
O	#	43.22	42.79	42.83	43.35	35.56	29.58
Content		Figure 4a Diatom Coccus B. Salt	Figure 4b Diatom Clays Salt, Gypsum	# Diatom Coccus B. Filament	Figure 4c Diatom Clays Salt	# Diatom Clays Salt	Figure 4d # # Salt crystal

#: The element is not set up.

The solar salt crystal contains high Na, Mg, Cl, and Zr, attributed to sea water inclusion and radioactive contaminants. The solar salt with quadrilateral-dimensional crystals rich in Na and Cl was associated with small particles on the surface, suggesting radioactive dusts (Figure 4c).

3.5. Formation Processes of Microbial Mats on the Paddy Field after the FDNPP Accident

Microbial mats persisted as the primary visible evidence for life after serious damage by the radioactive contamination from the FDNPP accident that caused multiple pollution by tsunami and radionuclide exposure, after the 3.11 Earthquake (Figure 5). Salty microbial mats on the rice paddy soils at Karasuzaki, Minami-soma City, Fukushima were exposed to a radioactive situation. The microbial mats 2–3 mm thick subsequently developed high radiation levels of 0.62–1.1 micro Sv/h after 1–2 years, forming gypsum and halite on the surface (Table 3, point 1, Figure 4b). The SEM-EDS indicate compact associations with abundant microorganisms, such as diatoms, and bacteria in the severe environment. The SEM-EDS clearly indicated diatoms and clays with discernible concentrations of radionuclides, such as I, Cs, Ba, Nd, Th, U, and Np, indicating a capacity for adsorbing both radionuclides and stable isotope elements on/from radioactive-polluted paddy soils. The radioactivity (^{137}Cs, ^{90}Sr, ^{93}Zr) originated from the FDNPP accident.

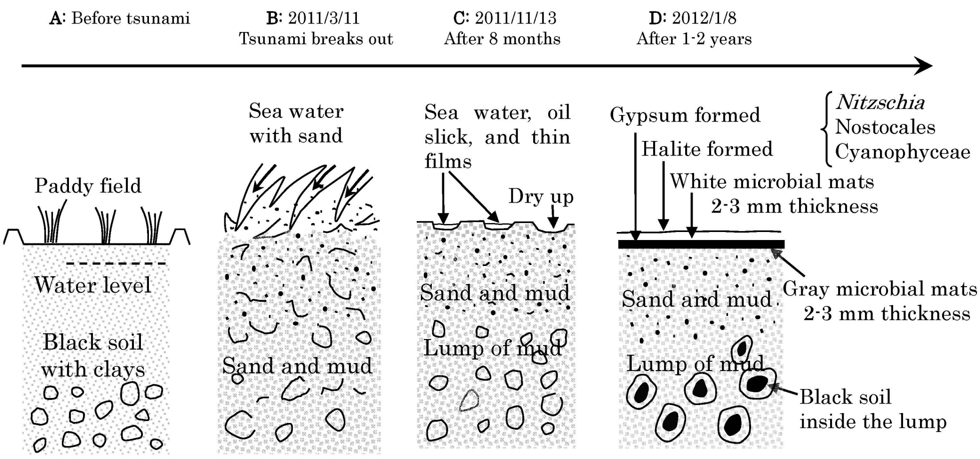

Figure 5. Schematic formation process of microbial mats with salt on the paddy soils after the FDNPP accident and tsunami in 2011.

4. Discussion

Microbial mats persisted as the primary visible evidence for life on Earth for almost three Ga. During this period, they would have been the dominant biological feature of life on the planet. Nonetheless, even today, they persist in special places such as thermal springs and high salinity environments where conditions are too extreme for extensive eukaryotic grazing [8]. Experiments in cultivating modern mats suggest that the time necessary for this transition encompasses several weeks of non-burial, although a thin mat may develop over beach or tidal flat sands within a matter of only *ca*. 8 h between a bi-diurnal ebb and the following flood [9]. They show the flood tides of siliciclastic peritidal systems on the modern Chandipur tidal flat, eastern coast of India, characterized by wide cracks with upturned margins [9]. Biodynamics of modern marine stromatolites and exopolymers (extracellular polymeric substances) can be seen in diatom-dominated marine sediment and bio-films on the surface of intertidal sediments [10–12].

4.1. Bio-Mineralization and Bio-Remediation

Filamentous fungi, yeasts, algae, bacteria, and diatoms have been evaluated for radioactive elements removal via bio-sorption. Microbial mats can accumulate heavy metals and radionuclides through precipitation and complexation on and within the cell surface containing hydroxyl and carboxyl groups. Diatoms, radiolarians, and foraminifera have mineral-forming species. They are widespread in the main sediment-forming organisms of the oceans, producing minerals as different as barite ($BaSO_4$), celestite ($SrSO_4$), and gypsum ($CaSO_4 \cdot 2H_2O$) [13]. Green sulfur bacteria use various reduced sulfur compounds such as sulfide, elemental sulfur, and thiosulfate as electron donors for photoautotrophic growth. The inorganic sulfur oxidizing systems of these bacteria with emphasis on the biochemical aspects were reported by Sakurai *et al.* [14].

In this study, as the microbial mats were 10–100 times more radioactive than the surrounding groundwater, indications of microbial immobilization of radionuclides are shown in Tables and Figures. The microbial mats on the surface of paddy fields with pH 8.1, 32.7 °C, salinity 27 ‰, air dose rate 0.59 μSv/h, microbial mat dosage 1.05 μSv/h (surface) and 0.48 μSv/h (reverse) on 15 September 2012, in Karasuzaki, Minami-soma City, Fukushima, forming the minerals of sulfur-bearing compounds of gypsum ($CaSO_4 \cdot 2H_2O$) and halite (NaCl) (Figures 3 and 4). Diatom cells were spherical grains of 100–200 nm in diameter (Figure 4).

The XRD results (Figure 3) were shown to be of gypsum whereas barite and celestite also are possible to be formed, according to XRF and SEM-EDS results (Tables 1 and 3), showing that Ba and Sr contents per unit would not contribute much to the whole XRD analysis. The

SEM-EDS elemental content maps clearly indicated Sr concentrated in the diatom cell and gypsum (Figure 4a,b,c,d). It would seem that all of these alkaline earth sulfate crystals occur inside membrane-bounded vesicles.

A role for Zr (both radionuclide and/or stable isotope) as an essential nutrient for the mineral-forming species has not yet been established. A similar silica deposition vesicle occurs in diatoms and there is good evidence to show that active transport processes are involved with the uptake of silicic acid and radionuclides. Siliceous skeletons are formed of amorphous silica. Generally, microbial mats at about 30–50 °C, consisting mainly of mono-cellular diatoms that perform photosynthesis, are formed, and at even lower temperatures the diatoms begin to diversify with eukaryotic diatoms forming microbial mats [15]. In addition to organic substances, the chemical structure of the large micrococci is thought to consist mainly of Si, P, S, and Ca components, though it displays a small amount of Na, Mg, Al, Cl, and K, and some evidence of Fe and Cu (Tables 1 and 3 Figure 4). The formation process of microbial mats on the paddy field with abundant diatoms and microorganisms can take up radioactive components with seawater elements as nutrients for growth and forming minerals after 1–2 years of experimental demonstration (Figure 5**)**.

On laboratory aqueous examination, using diatomaceous earth in Noto, Ishikawa Prefecture in Japan, the results showed that clay of montmorillonite and diatom have the capability to absorb radionuclides. The experimental conditions were under strong acid pH 2 and high EC of 2500–3500 mS/cm, sharply increasing with experimental time of 174 h. After 10 months, the radioactive muddy water transferred to the top of the chunk, showing 140 cpm on the top whereas a dosage of 800 cpm was at the bottom. The diatomaceous earth showed high capabilities to adsorb radioactivity [3].

4.2. Source of Zirconium in the Microbial Mats and Salts

Zr has both stable isotopes (^{90}Zr 51.45%, ^{91}Zr 11.22%, ^{92}Zr 17.15%, ^{94}Zr 17.38%, and ^{96}Zr 2.80%) and radionuclides (^{93}Zr, ^{95}Zr, and ^{97}Zr), which are contained in $ZrSiO_4$ and ZrO_2 minerals in nature. The Zirconium can be used for coating materials of the fuel rods at nuclear power plants. Zirconium is stable under 900 °C, but reacts with water and produces ZrO_2 associated with hydrogen gas above 900 °C [16]. The cause of the FDNPP accident was a hydrogen explosion, which caused Zr to be scattered to the air. The size of the scattered particles in the formed spherical dust is 2 µm in diameter [17]. FDNPP leaked 17 kinds of radionuclides, such as ^{134}Cs, ^{137}Cs, ^{90}Sr, and ^{95}Zr to the atmosphere and seawater in Japan [2].

In this study, we recognized the presence of high concentrations of Zr in the microbial mats and salts, see XRF results in Table 1 and SEM-EDS analyses in Table 3. We found high concentrations of Zr (4.33%) in the solar salts (Figure 44d) made from sea water in Karasuzaki, Minami-soma City, Fukushima Prefecture, Japan. The XRF and SEM-EDS methods indicated total/ only radionuclide and stable isotope which cannot indicate the origin of the Zr. We need specific data, and unfortunately there are no data of radionuclides of ^{95}Zr (half-life time 64.0 days) nor ^{93}Zr (half-life time 1.5×10^6 year) in the world.

4.3. Radionuclide Sorption to Clays and Salt in Microbial Mats

Clay minerals are also a significant component of radioactive soils and tsunami sediments generated by the FDNPP accident on 11 March 2011. Cooling systems failed at the reactors, leading to a meltdown of nuclear fuel, and this released a significant quantity of radionuclides into the environment. Four years after the accident, the radioactive ^{137}Cs is now the major source of radiation in Fukushima Prefecture. In this XRD study, a 7 Å clay peak was found on the reverse of the microbial mats (Figure 3b).

Many researchers have suggested, mainly based on laboratory experiments, that clay minerals, such as micaceous minerals (biotite, muscovite, and phlogopite; 10Å) and vermiculite clays (14 Å), are important for the sorption and retention of Cs in the soils [6,18–20]. The radioactive soil particles were classified into three types from their morphologies and chemical compositions, using IP autoradiography and electron microscopy: (1) conglomerates of fine clay minerals, (2) organic matter containing clay mineral particles, and (3) weathered biotite with a platy shape originated from granite. The weathered biotite is actually a biotite-vermiculite mixed-layer mineral [7].

The background surrounding the bacteria is rich in Na and Cl because of the salty surface of paddy soils in Bahi for the dry season [21]. The environmental condition in Bahi, Tanzania is quite similar to Karasuzaki in Fukushima, Japan, after the tsunami and FDNPP accident, in this study. Evaporation is also an important agent in fresh water and sea water. Cyanobacterial calcification cannot be seen as an index of changes in sea-water chemistry and $CaCO_3$ precipitation rates, although having considerable importance for studies of marine geochemistry and carbonate sedimentation.

The interaction of soils with I, Cs, Te, Ag, Pu, and Sr pollutants is controlled by a complex interplay of surface organic chemistry, redox, pH, and microbiology [22]. Especially common is the adsorption of Cs and K onto the edge and interlayer sites of 7 Å clay minerals. Cesium (Cs) sorption experiments were conducted using the soil of a paddy field in Fukushima, to find Cs-sorption materials in the actual soil. The soil particles were reacted with a CsCl solution for one day, which formed a Cs distribution on the disk surface, acquired using electron-probe X-ray microanalysis and TEM. The major Cs-sorbing materials were biotite-vermiculite mixed-layer minerals and aluminous smectite containing considerable amounts of iron [22]. Their results suggested that the surface of the paddy soil particles in Minami-soma City, Fukushima reacted with sea water and radioactive materials quickly by the tsunami and the FDNPP accident on 11 March 2011, supporting results in this study.

The circulation and transportation of surface seawater at monitoring sites generally reflects a weathering, such as rain, wind, and dust of vertical and horizontal circulation [23]. Particularly in this case, the radionuclides were carried out by contaminated water from the FDNPP area to the coastal zone in this area.

However, other data of longer half-life time radionuclides, such as ^{90}Sr, ^{93,94,96}Zr and actinides (Th, U, Np, Pu) are very limited, and there is little information of long-distance transportation of contaminants of dusts and clay mineral particles by winds from FDNPP. We need these long-term data, which will serve as an aid to weather forecasts and understanding the climatic systems in the world.

5. Concluding Remarks

Although more than four and half years have passed since the accident at the FDNPP, radioactive ^{137}Cs remains as the main source of the high radioactivity in the environment of Karasuzaki, Minami-soma City, Fukushima, Japan.

The present investigation carried out here is summarized below.

(1) This study is probably the first one to identify materials that can strongly absorb and retain radioactive elements in the actual paddy soils in Fukushima. The results suggest that microorganisms living in colonies constructed biofilms and microbial mats on the surface of paddy soils after the FDNPP accident and tsunami.

(2) Microorganisms responded with a metabolic reaction under radioactive and salty conditions, forming gypsum and halite showing the ability of microorganisms to grow in this contaminated environment and to immobilize radionuclides.

(3) The microorganisms inhabit each growing environment selectively forming microbial mats and t concentrate particular elements, such as radionuclides with salt.

(4) The solar salt made of sea water at Karasuzaki ocean bath, Minami-soma City, Fukushima, in 2015, shows a high Zr (4.33%) content associated with ^{137}Cs and ^{40}K without ^{131}I. The microbial mats have also accumulated Zr after the FDNPP accident and tsunami.

(5) It is possible that the capability of radioactive immobilization can be used to counteract the disastrous effects of radionuclide-polluted paddy soils.
(6) Their presence in the environment, therefore, is of use for mediating the risk of contaminated sites for longer periods of time, such as concentration of ^{90}Sr and ^{93,94,96}Zr on many different spatial and time scales and would benefit our global society.

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