CHEMIJA. 2016. Vol. 27. No. 3. P. 135–142

Long-time corrosion of metals (steel and aluminium) and profiles of fungi on their surface in outdoor environments in Lithuania

Albinas Lugauskas,

Gedvidas Bikulčius,

Dalia Bučinskienė,

Aušra Selskienė,

Vidas Pakštas,

Elena Binkauskienė*

Institute of Chemistry,
Center for Physical
Sciences and Technology,
Saulėtekio Ave. 3,
LT-10257 Vilnius, Lithuania

Outdoor corrosion investigations of low carbon steel and aluminium surfaces were performed from 2002 to 2012 in rural, marine and industrial sites on the territory of Lithuania. The morphological and structural changes of surfaces were evaluated using optical, scanning probe, scanning electron microscopy and wavelength dispersive X-ray fluorescence spectroscopy. The atmospheric corrosion level was determined using the mass loss method. This investigation has shown that the corrosion of steel and aluminium and diversity of fungi and their survival found on these materials differed depending on the exposure conditions. The highest mass losses were determined in the marine test site. The processes of the biodeterioration taking place on corroded metal surfaces are discussed. The most common culturable fungi at the end of exposure, both on steel and aluminium surfaces and in all regions, were *Chrysosporium merdarium, Paecilomyces parvus, Talaromyces flavus, Aureobasidium pullulans*, and partially *Cladosporium cladosporioides* and *C. herbarum*.

Keywords: steel, aluminium, exposure, mycobiota, corrosion

INTRODUCTION

Numerous studies have provided evidence that corrosion rates of metals under long-time outdoor exposure conditions are strongly influenced by the main atmospheric pollutants (sulphur dioxide, chloride ions and air-born nitrogen compounds) as well as by the atmosphere humidity and temperature [1].

The role of microorganisms has been not sufficiently studied particularly in the North Eastern region of Europe. Fungi can act on chemical biodeterioration through the action of their metabolic products (including organic acids, mycotoxins, and pigments). Transformation reactions of organic modify chemical and physical properties of metal and coating surfaces [2]. Because many metals are essential for fungal growth and metabolism, all of them can exert toxicity when present above certain threshold concentration in bioavailable forms. Metals that have no known biological function can also be accumulated and exhibit toxity. Toxicity is greatly affected by the physicochemical nature of the environment and the chemical behaviour of a particular metal and fungal species [3, 4].

A number of studies have shown that biogenic aerosols play important roles in atmospheric chemistry physics, the biosphere, climate and public health [5–10]. Dust emission strongly depends on the moisture level of the mechanically disturbed material. The moisture-holding capacity of the air is also important, and it correlates strongly with the surface structure.

The atmospheric corrosion of metals in Lithuania has not been previously systematically studied. The last decades studies of microbial adherence to different substrata led to the conclusion that the survival of microorganisms in the natural habitats is dependent on their capacity to adhere to different surfaces/substrata and to form biofilms. The total number of 161 species from 74 genera with different degrees of biofilm formation after one-year exposure of metals to rural (R), marine (M) and industrial (I) environments in Lithuania have been assessed [1, 11]. Sampling from different metal surfaces in different outdoor environments of Lithuania during long-time corrosion investigations from 2002 to 2012 was performed [9, 12].

According to Videla and Herrera [13], biocorrosion and its counter process (microbial inhibition) are rarely linked (to a single mechanism) to a single species of microorganisms.

---

* Corresponding author. E-mail: elenbink@ktl.mii.lt

The large study of effectiveness of selected airborne fungal species on corrosion of solid surfaces undermodelling conditions, as a prelude to recommended preventive measures, was performed [14]. Most of the previous investigations on individual fungus-induced effects on biomodified metal surface destruction were carried out in the nutrient medium by using contemporary technical means. The published study demonstrated a unique capability of the quartz crystal microbalance (QCM) to sense microbiological corrosion in situ. The results on the comparison of QCM data between the samples affected by *Aspergillus niger* and the abiotic ones showed a marked increase in aluminium electrode mass due to the development of a biofilm and microbiologically influenced corrosion. The data obtained are partly supported by the results obtained for the other fungi [15].

The attempt to quantify the influence of selected fungi to the extent of decomposition of metal surfaces has been made. For example, it was determined that *Penicillium frequentans*, *A. niger*, and *Bacillus mycoide* influenced the corrosion rate of metals. The method of electrochemical impedance spectroscopy measurements indicated the inner aluminium oxide layer and the other one, which develops due to the aluminium oxide layer interaction with the products of metabolism of microorganisms [16, 17].

A relation between the surface and interface fungal stimulated processes, the difference in consumption and production of microelements, which was caused by the growth of *P. palitans* 6 and *Arthrinium phaeospermum* 10 on steel, has been determined by X-ray fluorescence spectroscopy and X-ray diffraction microscopy [18].

The properties of electrically conducting polymers are close to those of metals and semiconductors. It is established that one of the extensively studied conducting polymers, polyaniline, can participate in fungal electron transfer [19, 20]. The comparison of biofilms formed by 9 different fungi on the polyaniline surface using cyclic voltammetry, X-ray photoelectron spectroscopy, scanning probe microscopy, and water contact angle measurements has shown that the rate of biofilm formation markedly differs and a conspicuous difference in the oxidation level, redox activity, oxalate impurities, catalytic properties, and biomineralization of the polyaniline surface was confirmed [21].

The results on investigation of zinc and copper atmospheric corrosion after long-time 10-year exposure in outdoor conditions of Lithuania have been published recently [12]. Different survival of mycobial communities and its impact on the structural properties of zinc and copper have been determined. It may be supposed that the determined nanostructural development of minerals and geopolymers hindered environmental aggressiveness to zinc and copper surfaces.

This paper focuses on outdoor corrosion of steel and aluminium, which are the constituents of construction materials of technical purpose used in the North Eastern region of Europe, and mycobiotical contaminants in the (R), (M) and (I) environments of Lithuania.

EXPERIMENTAL

Corrosion tests were conducted by exposing metal specimens (100 × 150 × 3 mm) of low carbon steel (0.5–0.12% C, 0.03–0.10% Cu, <0.07% P) and aluminium Al (99.4%). The specimens were exposed to natural environment for 10 years (from May 2002 to November 2012) in the following three sites on the territory of Lithuania: (Molėtai–Kulionys) rural (R), (Neringa–Preila) Baltic sea shore marine (M), (Vilnius–Visoriai) industrial (I). Specimens exposed to standard room conditions (HN 69:2003) were used as a reference (control, C).

The specimens were exposed on the south-oriented metallic stands and situated at an angle of 45° to the horizon. Corrosion evolution was performed according to the ISO standards [9223, 9224, 9225, and 9226]. At every climatic study stand 5 metal plates were exposed.

To determine the metal mass loss (Δm) due to corrosion, the products formed during the process were removed by using the methods and the procedure described in the ISO 8407:2014 standard. Removing of the corrosion products was carried out for as long as the obtained mass value matched the mass of non-corroded metal.

Biofilms sampling, fungi isolation and identification methods have been described in previous works [12, 21].

Morphological changes in metal surfaces were evaluated by using an optical microscope MMU-3 with a CCD camera at 55x magnification, the magnitude of the marker was 10 μm per 1 cm of the photograph, and a scanning probe microscope Explorer (VECO Topometrix, USA) and a scanning electron microscope EVO 50 EP (Carl Zeis SMT AG, Germany). The determined R_z is the maximum height of roughness profile (μm). The chemical analysis of metal samples was performed by the X-ray fluorescent spectroscopy with a wave dispersion (WDXRF) method. An Axios Max spectroscope (PANalytical, Holland, 2010) with a 4 kW Rh anode was used. Specimens were discs of 37 mm in diameter.

RESULTS AND DISCUSSION

Δm measurements provided the most reliable indicator of the corrosion behaviour of metals. As seen from Fig. 1, the corrosion behaviour depends on the type of metals and environments. The highest Δm values under natural exposure conditions were determined in the (M) test site. This is apparently determined by the differences in meteorological factors and atmosphere pollution, especially a higher concentration of chlorine ions. Taking into account the windiness, it may be stated that the surface of the samples is moistened and dried more often in the (M) environment and the corrosion products are washed away more often too.

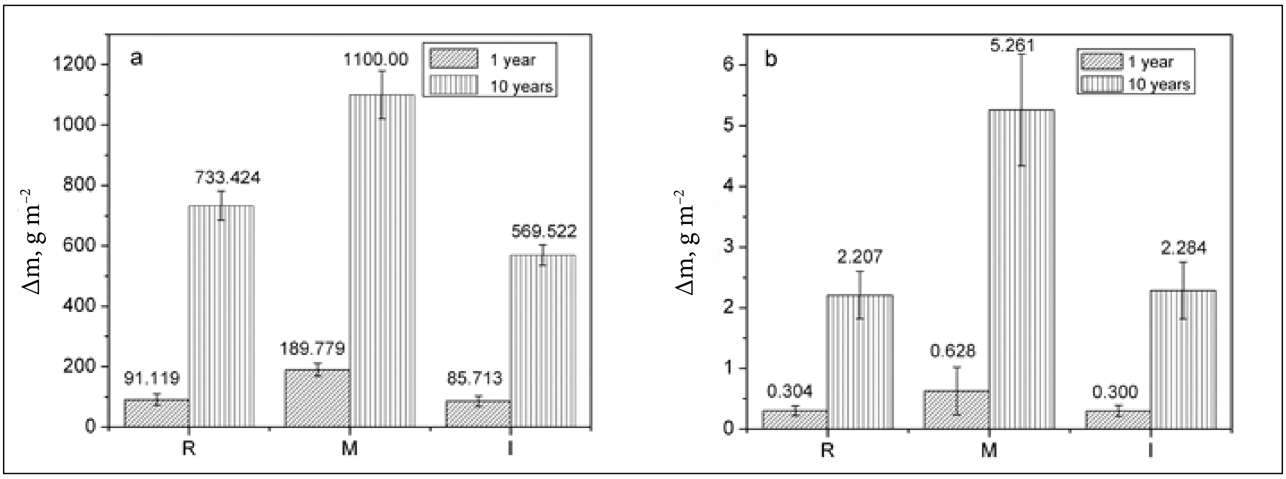

Fig. 1. Mass losses (Δm) of steel (a) and aluminium (b) after 1 and 10 years of exposure to rural (R), marine (M) and industrial (I) environments

The morphological investigations by the scanning probe microscopy (SPM) method have determined that shell-like structures up to 150 μm in diameter are observed on the surface of steel plates exposed to the (R) environment (Fig. 2, 1b). On the steel plates exposed to the (M) environment clusters of globules bonded into strings of the same origin from 0.5 to 10 μm in diameter were seen, alongside derivatives consisting of globules 15 μm in diameter were observed. The surface

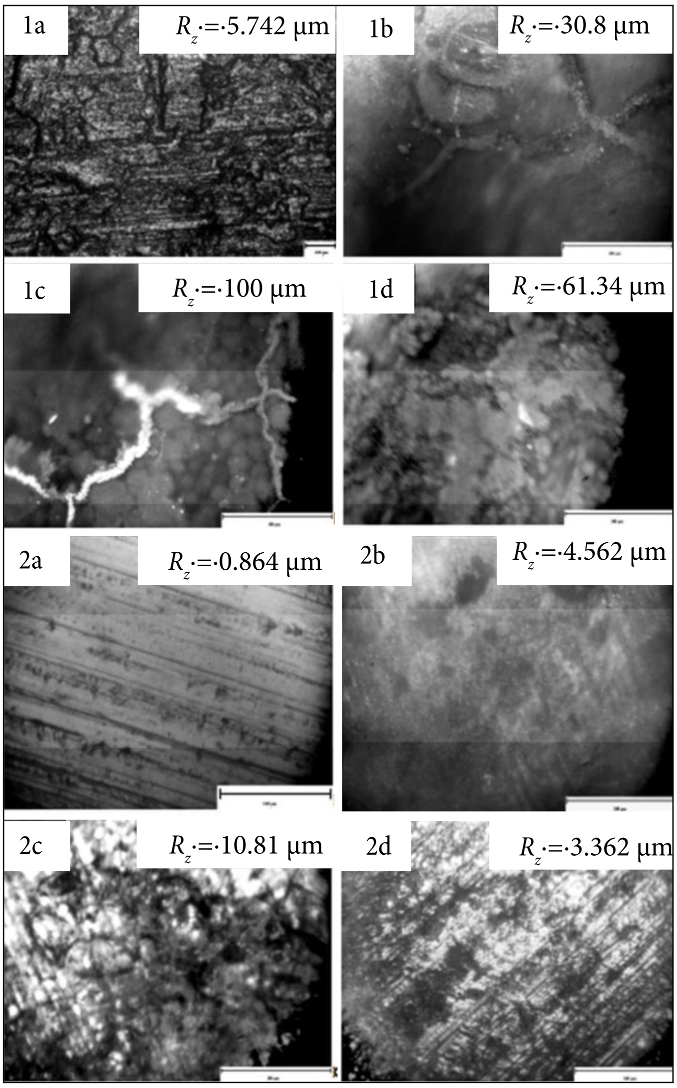

Fig. 2. SPM views of steel (1) and aluminium (2) surfaces after 10 years of exposure to: reference samples (1a, 2a), (R) rural (1b, 2b), (M) marine (1c, 2c), and (I) industrial environments (1d, 2d)

roughness exceeded 100 μm and we failed to measure it precisely, because this was out of the potentialities of the device (Fig. 2, 1c). On the surface of the steel plates which were exposed to the (I) environment (Fig. 2, 1d) flat derivatives of an indeterminate shape of 50 to 100 μm in diameter as well as fine 2 to 5 μm corrosion splinters were seen.

The surface of aluminium plates under different environmental conditions changed differently. On the surfaces of aluminium plates which were exposed to the (R) environmental conditions coverings were present (Fig. 2, 2b). We can see dark spots, likely as deep cover, coming into being because of influence under bioagents and metabolites of their functions. The surfaces of aluminium plates exposed to (M) environmental conditions were granular and with dark spots (15 μm in diameter) (Fig. 2, 2c). The surfaces of aluminium plates which were exposed to the (I) environmental conditions were covered with small granules (3–7 μm) (Fig. 2, 2d).

An evaluation of the corrosion process dynamics, variations on the Δm parameter after 1 and 10 years of exposition, and SPM data obtained for steel and aluminium surfaces after 10 years of exposure are presented in Table 1. The values $\Delta m_{10}/\Delta m_1$ (Δm_1 and Δm_{10} are mass losses after 1 and 10 years of exposure) showed that the corrosion intensity was out of proportion to the studied period of exposition. The values $\Delta m_{10}/R_z$ showed that the corrosion of steel and aluminium differed depending on the exposure conditions.

A general view of the changes in the surface of steel and aluminium plates after 10 years of exposure to different environmental conditions is shown in Fig. 3. Mycobiota

Table 1. **Variations on the Δm parameter after 1 and 10 years of exposure and SPM data obtained for steel and aluminium surfaces after 10 years of exposure to rural (R), marine (M) and industrial (I) environments**

Metals	Environments	Δm_{10}, g m^{-2}	Δm_1, g m^{-2}	$\Delta m_{10}/\Delta m_1$	R_z, μm	$\Delta m_{10}/R_z$, g m^{-2}/μm
Steel	(R)	733.400	91.100	8.050	30.80	23.812
	(M)	1100.000	189.800	5.796	>100	<11
	(I)	569.500	85.700	6.645	61.34	9.284
Al	(R)	2.207	0.304	7.260	4.56	0.484
	(M)	5.261	0.628	8.377	10.81	0.487
	(I)	2.284	0.300	7.613	3.36	0.680

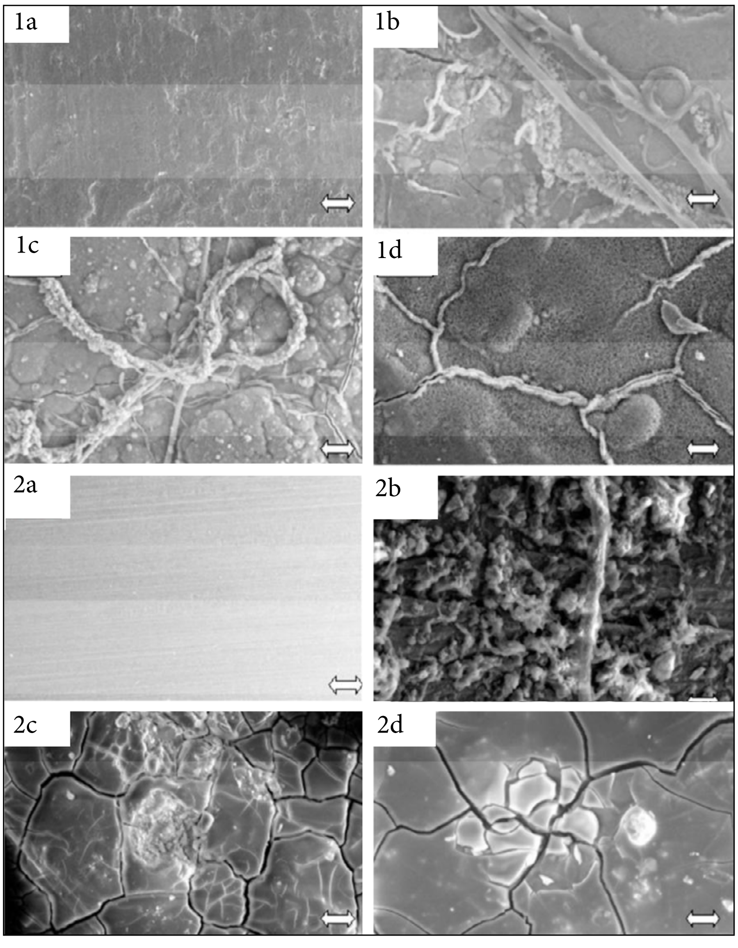

Fig. 3. General views of the changes on steel (1) and aluminium (2) surfaces after 10 years of exposure to: reference samples (1a, 2a), (R) rural (1b, 2b), (M) marine (1c, 2c), and (I) industrial environments (1d, 2d). Each scale bar corresponds to 20 μm

and their metabolites, whose mycelium hiphae are closely adherent to the surface of corroded steel plates, are interrelated (Fig. 3, 1b, c, d). In aluminium variants we can see only their separate propagules (Fig. 3, 2b, c, d). A wider variety of different propagules on the aluminium surface was formed in the (M) environment (Fig. 3, 2c).

Changes in the elemental composition of steel and aluminium surfaces after 10 years of exposure were determined by using the WDXRF method and are presented in Table 2. The distribution of elements occurring on the corroded steel and aluminium surfaces in the logarithmic scale is shown in Fig. 4. Changes in the elemental composition modify the physical properties and redox properties of metal and coating surfaces [22, 23]. The analysis of the data has shown that the elemental composition of the surfaces of plates exposed to (R), (M) and (I) environments markedly differs from that of the reference plate (C). Differently from aluminium on all the exposed steel plates a marked increase of oxygen quantities was observed. That confirmed a marked steel corrosion detected by Δm measurements (Fig. 1). On the surface of all the exposed aluminium plates the stronger tendency of increasing of biogenic microelements (calcium, phosphorus, sulphur) can be observed. A slight agreement between increasing of calcium quantities (Fig. 4) and the Δm level (Fig. 1) detected biological mineralization impact on aluminium surface deterioration.

When several fungi are present on the metal surface, synergies or antagonisms may occur between them. Mycobiota with competitive advantages, allowing them to become the dominating species at the metal surface, are determined. The variety of fungi (Table 3) detected on steel and aluminium plates in the final stage of our 10-year experiments (November 2012) is compared to the results of the work performed under the same conditions after 1-year exposure published earlier [1, 11].

The physiological features of the fungal strains isolated from the substrates evaluate their potential for biodeterioration. The data obtained have shown that *Ch. merdarium* (the frequence of detection on steel after 1 year (R)-2, (M)-4, (I)-4, after 10 years (R)-9, (M)-9, (I)-9% and on aluminium after 1 year (R)-2, (M)-4, after 10 years (R)-9, (M)-9%), *P. parvus* (on steel after 1 year (R)-12, after 10 years 11%), yeast-like fungus *A. pullulans* (on steel after 1 year (M)-6, after 10 years 7%), *T. flavus* (on steel after 1 year (M)-4, after 10 years 4% and on aluminium after 1 year (R)-2, (M)-4, after 10 years (R)-9, (M)-9%), *C. cladosporioides* (on steel after 1 year (I)-28, after 10 years 7% and on aluminium after 1 year (I)-28, after 10 years 11%), *C. herbarum* (on aluminium after 1 year (I)-22, after 10 years 5%), *A. alternaria* (on aluminium after 1 year (I)-34, after 10 years 6%) have survived.

As you can see, a reduction in the species fungi colony has been detected on the aluminium plates exposed to the (I) environment for 10 years in comparison to 1 year. Compared to (M) and (R) environments, the higher values of $\Delta m_{10}/R_z$ (Table 1) may be assigned to the tendency to reduce the fungi concentration in the (I) environment on the aluminium surface.

Table 2. **The quantity of elements on steel and aluminium after 10 years of exposure to rural (R), marine (M) and industrial (I) environments, wt-%**

Elements	**Environments**							
	Reference (C)		**(R)**		**(M)**		**(I)**	
	Steel	**Al**	**Steel**	**Al**	**Steel**	**Al**	**Steel**	**Al**
O	1.690	3.280	35.30	12.10	36.10	22.40	35.20	16.90
Na	0.051	0.047	0.027	0.122	0.047	0.114	0.027	0.135
Mg	0.007	0.027	0.010	0.043	0.071	0.070	0.016	0.023
Al	0.058	95.7	0.025	84.9	0.157	74.2	0.044	80.2
Si	0.058	0.276	0.035	0.906	0.369	1.23	0.096	1.02
P	0.020	0.006	0.003	0.425	0.051	0.651	0.007	0.566
S	0.026	0.007	0.080	0.338	0.105	0.868	0.169	0.561
Cl	0.011	0.044	0.034	0.192	0.051	0.116	0.047	0.122
Cr	0.028	0	0.006	0	0.007	0	0.007	0
Mn	0.341	0.008	0.253	0.003	0.164	0.005	0.248	0.005
Fe	97.6	0	64.2	0	62.7	0	64.0	0
Ni	0.042	0	0.027	0	0.017	0	0.022	0
Cu	0.052	0	0.009	0	0.021	0	0.016	0
K	0	0.009	0	0.057	0	0.041	0	0.044
Ca	0	0.005	0	0.023	0	0.014	0	0.022
Ti	0	0.008	0	0.018	0	0.011	0	0.014

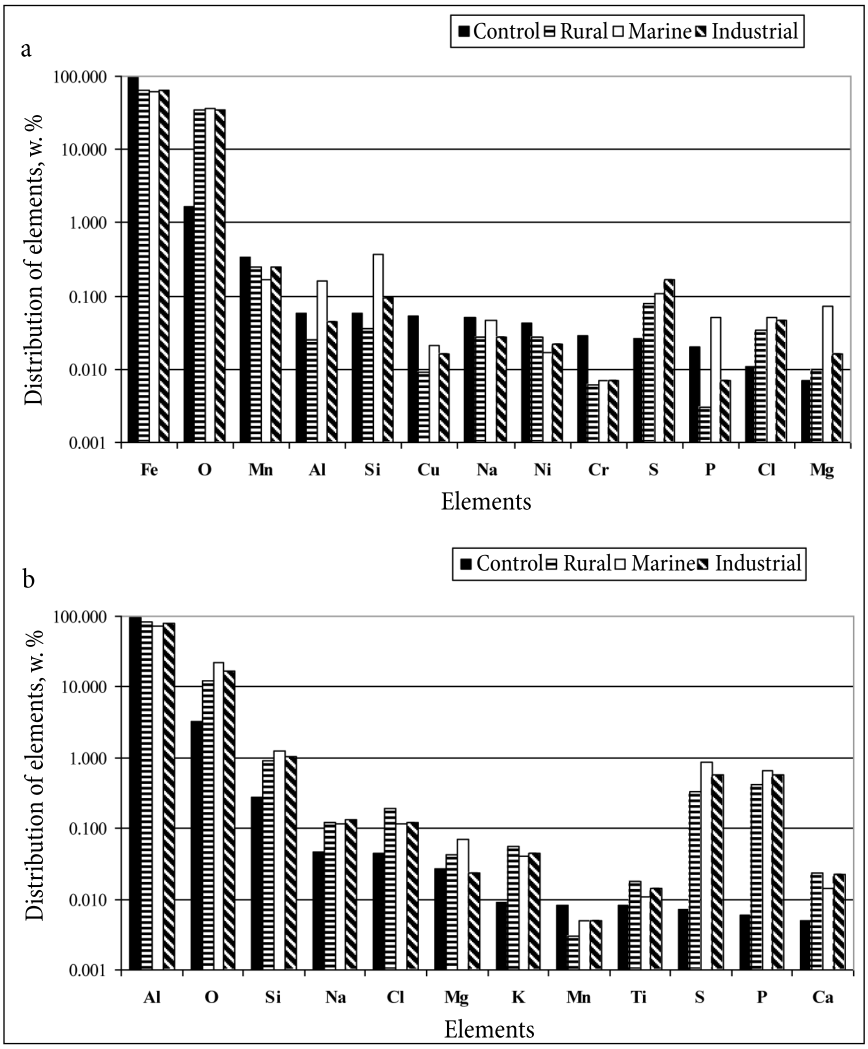

Fig. 4. Distribution of elements on steel (a) and aluminium (b) surface after 10 years of exposure to rural (R), marine (M) and industrial (I) environments, reference sample (C), wt-%

Table 3. **Detected fungi species on the surface of steel and aluminium plates after 10 years of exposure to rural (R), marine (M) and industrial (I) environments, new deposited (X) and survived (Y) fungi**

Fungi species	Steel			Al		
	Environments					
	R	M	I	R	M	I
Acremonium strictum	X	X				
Aspergillus ustus		X				
Aureobasidium pullulans		Y			Y	
Acremonium fusidicides					X	
Acremonium chorticola					X	
Alternaria alternata					Y	Y
Alternaria dianthi						X
Chrysosporium merdarium	Y	Y	Y	Y	Y	
Candida albicans			X		X	
Cladosporium cladosporioides			Y		Y	X
Cladosporium herbarum			Y			Y
Cladosporium sphaerospermum					Y	
Oidiodendron echinulatum			X			
Paecilomyces lilacinus	X					

Table 3 **(continued)**

Fungi species	**Steel**			**Al**		
	Environments					
	R	**M**	**I**	**R**	**M**	**I**
Paecilomyces parvus	Y			Y	Y	
Penicillium commune	X					
Penicillium expansum	X					
Penicillium varians				X		
Penicillium venetum	X					
Penicillium verrucosum					X	
Phialophora americana	X					
Phoma betae				X		
Phoma exiqua				X		
Phomopsis cinerescens				X		
Sclerotinia sclerotiorum					Y	
Scopuliariopsis brumptii					X	
Sporotrichum olivaceum	X			X		
Talaromyces flavus		Y	Y		Y	Y
Torulomyces lagena		X				
Ulocladium botrytis		X				
Verticillium alloatrum					X	
Mycelia sterilia	Y	Y	Y	Y	Y	Y

On steel in (I) and on aluminium in (M) environments yeast-like fungus Candida was isolated. *Candida* sp. is one of the common causes of nosocomial infections, the morbidity and mortality due to Candida infections being high alarmingly [24, 25]. It was described earlier that the yeast-like fungus, identified as *Candida* sp., was also recovered from the another metal surface [9, 12]. The data presented have shown that in all the variants of experiments sterile whitish-yellowish brown micelia *Micelia sterilia* grew from which reproductive organs characteristic of some fungi species may be formed. The study provides public health practitioners with comparative information on common culturable fungi in Lithuania.

CONCLUSIONS

We examined the corrosion of steel and aluminium samples after 10 years of exposure to different conditions of natural environment in Lithuania. The highest mass losses were determined in the (M) test site. The process of biodeterioration taking place on corroded metal surfaces is discussed. The ability of *Ch. merdarium, P. parvus, yeast-like fungus A. pullulans, T. flavus*, partially *C. cladosporioides* and *C. herbarum* to survive in (R), (M) and (I) environments has been determined. *Candida* was identified on corroded steel and aluminium surfaces in some environmental sites.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. I. Prosyčevas for his permission to provide the data of morphologic studies.

Received 20 April 2016
Accepted 10 May 2016

References

1. R. Ramanauskas, E. Juzeliūnas, A. Narkevičius, et al., *Chemija*, **16(1)**, 25 (2005).
2. E. Binkauskienė, *J. Chem. Tech. Biotechnol.*, **70**, 106 (1997).
3. G. M. Gadd, *Mycol. Res.*, **111**, 3 (2007).
4. A. Lugauskas, D. Pečiulytė, R. Ramanauskas, D. Bučinskienė, A. Narkevičius, V. Ulevičius, *Ekologija*, **1**, 11 (2005) [in Lithuanian].
5. V. P. Kurup, H. D. Shen, B. Banerjee, *Microbes Infect.*, **2**, 1101 (2000).
6. S. Maruthamuthu, N. Muthukumar, M. Natesan, N. Palaniswamy, *Current Sci.*, **94**, 359 (2008).
7. H. A. Videla, L. K. Herrera, *Int. Microbiol.*, **8**, 169 (2005).
8 W. Elbert, P. E. Taylor, M. O. Andreae, U. Pöshl, *Atmospheric Chem. Phys.*, **7**, 4569 (2007).
9. A. Lugauskas, I. Prosyčevas, A. Narkevičius, et al., *J. Environ. Eng. Landsc. Manag.*, **21**, 199 (2013).

10. A. Lugauskas, I. Prosyčevas, R. Ramanauskas, A. Grigucevičienė, A. Selskienė, V. Pakštas, *Materials Sci. (Medžiagotyra)*, **15**, 224 (2009).
11. A. Lugauskas, D. Bridžiuvienė, A. Narkevičius, E. Ivaškevič, *Mycol. Phytopathol.*, **38**, 54 (2004).
12. A. Lugauskas, G. Bikulčius, D. Bučinskienė, A. Selskienė, V. Pakštas, E. Binkauskienė, *Chemija*, **26(4)**, 219 (2015).
13. H. A. Videla, L. K. Herrera, *Int. Biodeterior. Biodegrad.*, **63**, 896 (2009).
14. A. Lugauskas, K. Leinartas, A. Grigucevičienė, A. Sielskienė, E. Binkauskienė, *Ekologija*, **54(3)**, 149 (2008).
15. P. Miečinskas, K. Leinartas, V. Uksienė, A. Lugauskas, R. Ramanauskas, E. Juzeliūnas, *Chemija*, **17(4)**, 30 (2006).
16. E. Juzeliūnas, R. Ramanauskas, A. Lugauskas, M. Samulevičienė, K. Leinartas, *Electrochem. Commun.*, **7**, 305 (2005).
17. E. Juzeliūnas, R. Ramanauskas, A. Lugauskas, et al., *Corros. Sci.*, **49**, 4098 (2007).
18. E. Binkauskiene, A. Lugauskas, I. Prosyčevas, et al., *J. Surf. Eng. Mater. Adv. Technol.*, **4**, 242 (2014).
19. E. Binkauskienė, V. Jasulaitienė, A. Lugauskas, *Materials Sci. (Medžiagotyra)*, **14**, 134 (2008).
20. E. Binkauskienė, V. Jasulaitienė, A. Lugauskas, *Synth. Met.*, **159**, 1365 (2009).
21. E. Binkauskienė, A. Lugauskas, V. Bukauskas, *Surf. Interface Anal.*, **45**, 1792 (2013).
22. E. V. Binkauskene, *Russ. J. Appl. Chem.*, **78**, 565 (2005).
23. E. Binkauskiene, B. J. Binkauskas, *Polym. Int.*, **58**, 869 (2009).
24. V. Lazăr, M. C. Chifiriuc, *Roum. Arch. Microbiol. Immunol.*, **69**, 125 (2010).
25. S. Hawser, K. Islam, in: J. L. Pace, M. Rupp, R. G. Finch (eds.), *Candida. Biofilms, Infection and Antimicrobial Therapy*, P. 171, Taylor & Francis Group, Boca Raton, FL (2006).

Albinas Lugauskas, Gedvidas Bikulčius,
Dalia Bučinskienė, Aušra Selskienė, Vidas Pakštas,
Elena Binkauskienė

METALŲ (PLIENO IR ALIUMINIO) KOROZIJOS IR PAVIRŠIUJE ESANČIŲ MIKOBIOTŲ RŪŠIŲ ĮVAIROVĖS ĮVERTINIMAS LIETUVOS APLINKOS SĄLYGOMIS

Santrauka

Mažaanglio plieno ir aliuminio bandinių korozinis pažeidimas įvertintas po dešimties metų (2002–2012) laikotarpio veikiant skirtingoms Lietuvos aplinkos sąlygoms. Nustatyta, kad korozinis pažeidimas ir mikobiotų rūšių įvairovė ant plieno ir aliuminio paviršių priklausė nuo aplinkos, kurioje jie buvo (agrarinėje, jūrinėje, pramoninėje). Morfologiniai ir struktūriniai paviršiaus pokyčių tyrimai atlikti naudojant optinį, skenuojančiojo zondo ir skenuojantį elektroninį mikroskopus bei rentgeno fluorescencinės spektroskopijos su bangų dispersija metodą. Atmosferinės korozijos laipsnis įvertintas masės netekties metodu. Labiausiai pažeisti bandiniai buvo jūrinėje aplinkoje. Darbe aptariamas tirtųjų paviršių biologinis pažeidimas minėtomis aplinkos sąlygomis. Labiausiai paplitę mikobiotai ant abiejų metalų paviršių visomis aplinkos sąlygomis buvo *Chrysosporium merdarium, Paecilomyces parvus, Talaromyces flavus, Aureobasidium pullulans,* iš dalies *Cladosporium cladosporioides* ir *C. herbarum.*