

## Supporting Information for

### Corrosion behavior of 316L and 304 stainless steels exposed to Industrial-Marine-Urban environment: Field Study

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## 1. Measurement of Atmospheric Corrosion Parameters

### 1.1 Preparation of Wet Candle for Chloride Determination

The procedure mentioned in ASTM G 140-02<sup>1</sup> (2002) was adopted for preparation and assembly of wet candle apparatus using Erlen Meyer flask, glass test tube, solid rubber, cotton bandage gauze (Fig. 3). Type IV reagent water was prepared as follows: 200 ml glycerin and 20 drops of octanoic acid were added in 1L of water. The octanoic acid was added to prevent freezing during the winter season. The apparatus was exposed for 30 days and the chloride content was estimated against AgNO<sub>3</sub> by titration.

The following equation was used to calculate the chloride content

$$\text{mg Cl}^-/\text{L} = (\text{ml AgNO}_3 \text{ used} - B) \times T \times 1000/\text{ml specimen} \quad (1.1)$$

where T is titre, mgCl<sup>-</sup>/ml of AgNO<sub>3</sub>, B- Indicator blank.

The determined chloride content in the atmosphere is reported as mg Cl<sup>-</sup>/m<sup>2</sup>/day.

### 1.1.2 Preparation of Sulphation Plate for the Determination of SO<sub>2</sub>

Wattmann Filter papers (grade 30) were cut and placed at the bottom of polystyrene culture dishes. Paper is bonded to the plate by adding acetone until the filter paper becomes saturated. Acetone is allowed to evaporate. Polystyrene plates were rinsed with distilled water. 900 ml of distilled H<sub>2</sub>O, 3.5 g of gum tragacanth was added and blended for 2 h. From this solution, 350 ml was taken and then about 3.5 g pulp of filter paper was added to that mixer solution. Further about 112 g of lead peroxide (PbO<sub>2</sub>) was added to the same solution and blend for 2 min. 10 ml of the mixture was pipetted out carefully into the plate and ensured for the uniform spreading through the water layer in the plate. The plates were placed in oven and heated at 40 to

50 °C for 20 h. The plates were removed from oven and allowed to cool. They were sealed with tight fitting covers to preserve until the exposure begins. The sulphation plates were exposed for 30 day intervals time. The plates were recovered and analyzed for the SO<sub>2</sub> content. Barium sulphate (BaSO<sub>4</sub>) precipitation by gravimetric analysis was used and the sulfate analysis provided the quantity of sulfate present on each disc (Fig. S3). Using the following equation SO<sub>2</sub> capture rate was determined and further from it, SO<sub>2</sub> content in the exposed environment are reported. The above described sulphation plate were prepared by following the ASTM G 91-97<sup>2</sup> (1997) procedure.

$$R = (m - m_0) \times MWSO_2 / MWSO_4 \times A \times T \quad (1.2)$$

where  $m$  is the mass of sulphate found in the plate, in mg,  $m_0$  is the mass of sulfate found in blank (unexposed) plate, in mg,  $MWSO_2 = 64$ ,  $MWSO_4 = 96$ ,  $A =$  Area of the plate,  $m^2$   $T =$  exposure time of the plate, days,  $R =$  SO<sub>2</sub> capture rate, mg SO<sub>2</sub>/m<sup>2</sup> /day

### 1.1.3 Gravimetric Weight-Loss Analysis and Determination of Corrosion Rate

The exposed samples were removed from the stand and the initial weights were measured. The corrosion products of SS were removed by immersion in etching solution as specified in ASTM G1-99<sup>3</sup> (1999). The etching solution was prepared as follows: 100 ml of HNO<sub>3</sub> was added to 1000 ml of distilled water. The exposed SS specimens were immersed for 20 minutes at 60 °C to remove the corrosion products. The final weight was measured after removing the corrosion products. From the initial and final weights, the corrosion rate in mpy was calculated using the following formula,

$$\text{Corrosion rate in mpy} = k \times w / D A T \quad (1.3)$$

where,  $k$  = constant ( $3.45 \times 10^6$ ),  $w$  = mass loss, mg,  $D$  = Density of SS, g/cm<sup>3</sup>,  $A$  = area, cm<sup>2</sup>,  $T$  = Time of exposure in hours.

## 1.2 Surface Characterization of Exposed Steels

### 1.2.1 Raman Spectroscopic Studies

Raman spectra of rust layers were obtained from the corrosion products of the atmospheric exposed steels using the Almega dispersive instrument with the He-Ne 532 nm wavelength on the rust layers. The compounds in rust layers exist as mixture of iron oxides and oxyhydroxides as intimate mixtures with their own strong structural relationships. Hence, the conversion of one phase to another phase is very feasible either by electrochemical redox reactions, heating in under laser radiation. These treatments can cause the de-hydroxylation or oxidation of the corrosion products ( $\alpha$ ,  $\beta$ ,  $\gamma$ -FeOOH and Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>), in particular magnetite is highly sensitive to laser irradiation which is disadvantageous for obtaining good Raman signal. To overcome this we used a set of six density filters to modulate the laser power on the sample from 5.2 mW to 5  $\mu$ W. With this precaution, all identified phases presented stable Raman spectra checked at a power of 0.65  $\mu$ W.<sup>4-6</sup> The Nikon microscope was used to monitor the analyzing spot at the

magnification of 50  $\mu\text{m}$ . The sampling stage equipped with the motorized platform joy stick to move to the desired location of the spot.

### **1.2.2 Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray (EDAX) Analysis**

The microstructure and elemental distributions in the rust layers were analyzed using a Quanta 200 FEG SEM equipped with energy dispersive X-ray analysis (SEM-EDAX) facilities. The microstructure and elemental distributions in the rust were analyzed before grinding using Quanta 200 FEG scanning electron microscope (SEM). The 2D line profiles of SEM images were obtained using the scanning probe image processor WSxM 5.0 develop 7.0 software.

### **1.2.3 Vicker's Micro-Hardness Measurement**

The Vicker's micro-hardness of bare and exposed stainless steels were measured using micro-hardness testing system (Fischer scope H100C). The hardness profile of the surface was measured with constant load at 200 mN (10 points / specimen). The loading and unloading time was taken as 10 seconds to investigate the mechanical behaviour of the stainless steels after exposing to the IMU environment during field study.

### **1.2.4 X-ray Fluorescence Analysis**

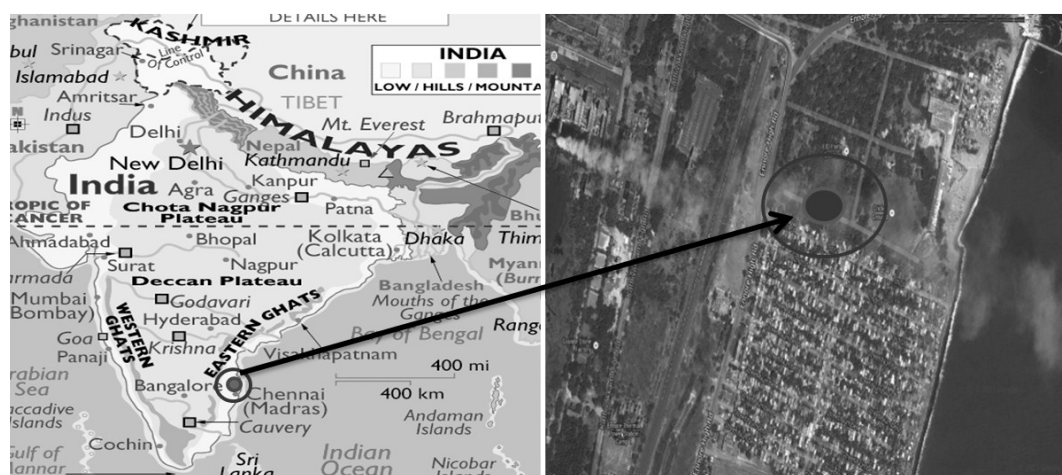
The elemental chemical composition of the stainless steels and the corrosive agents viz., Cl and S were analyzed semi quantitatively using Shimadzu XRF-1800 fluorescence analyzer.

## 2. Additional Figures



**Fig. S1** Photographs of various steels in the exposure rack at the exposure site Chennai

### Exposure Site



**Fig. S2** Topography of the location of atmospheric corrosion exposure site of Chennai

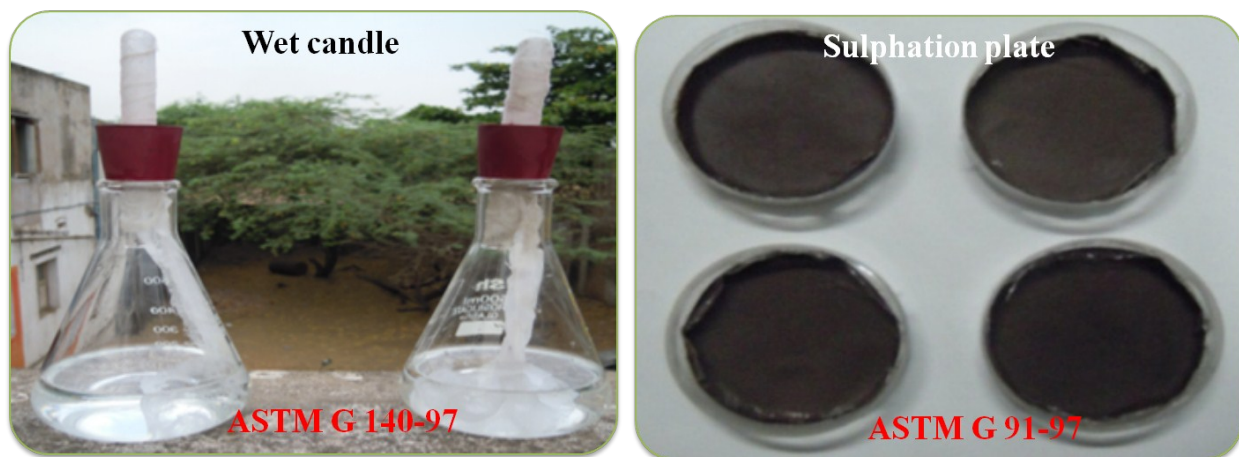
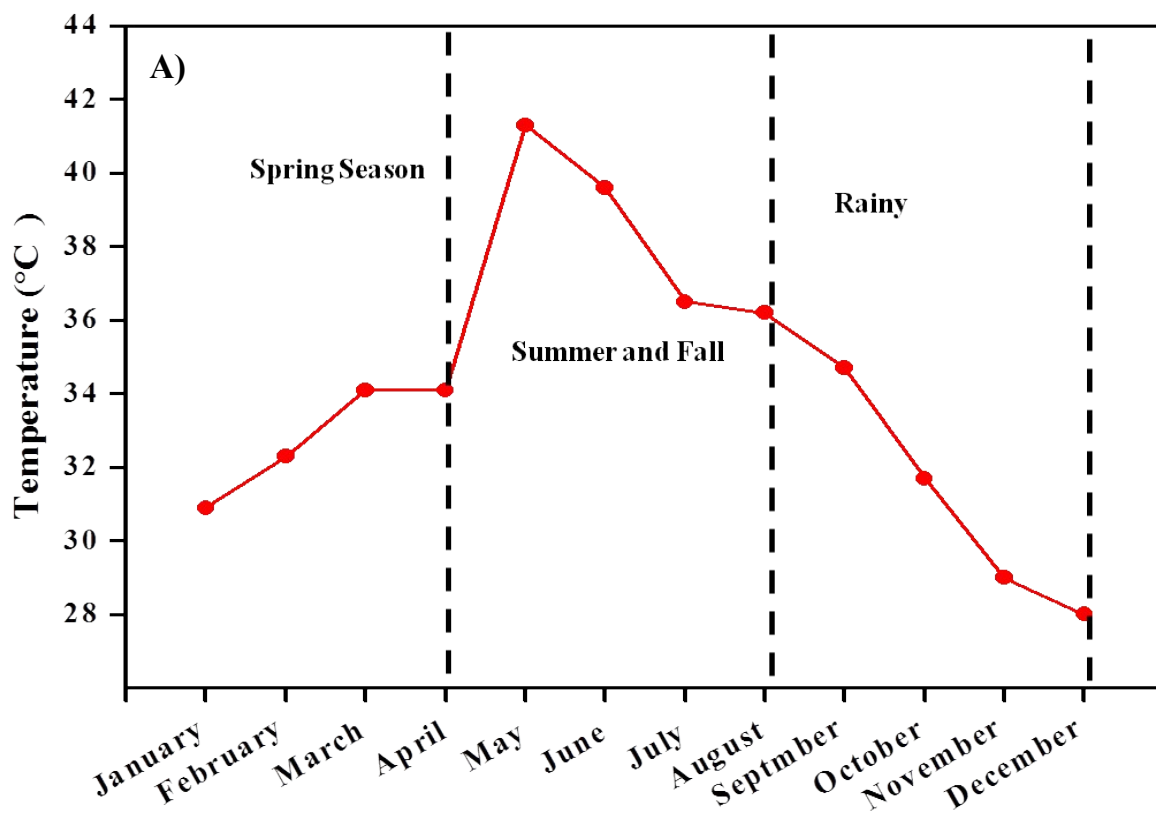
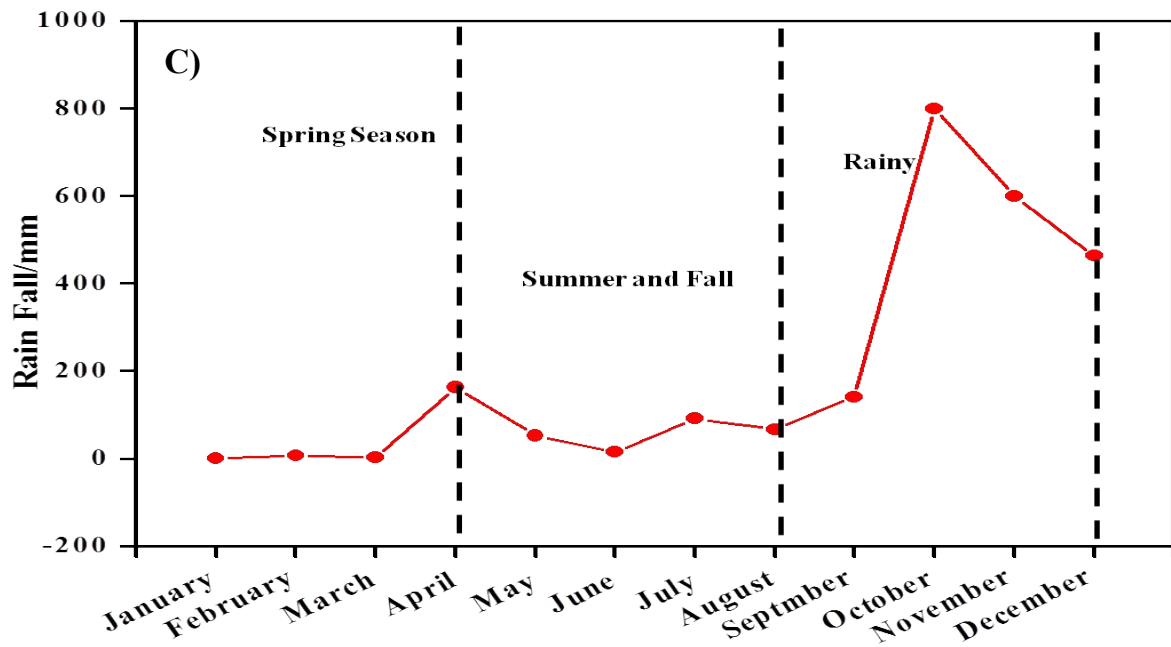
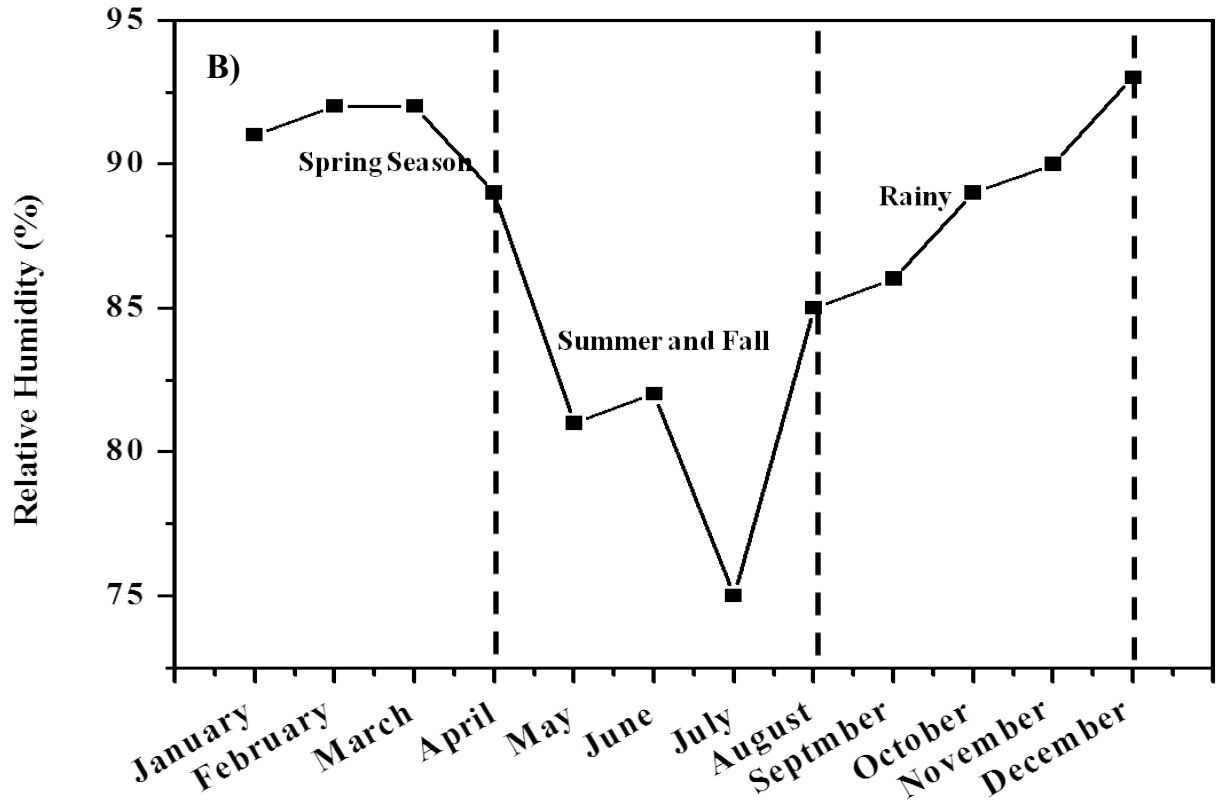
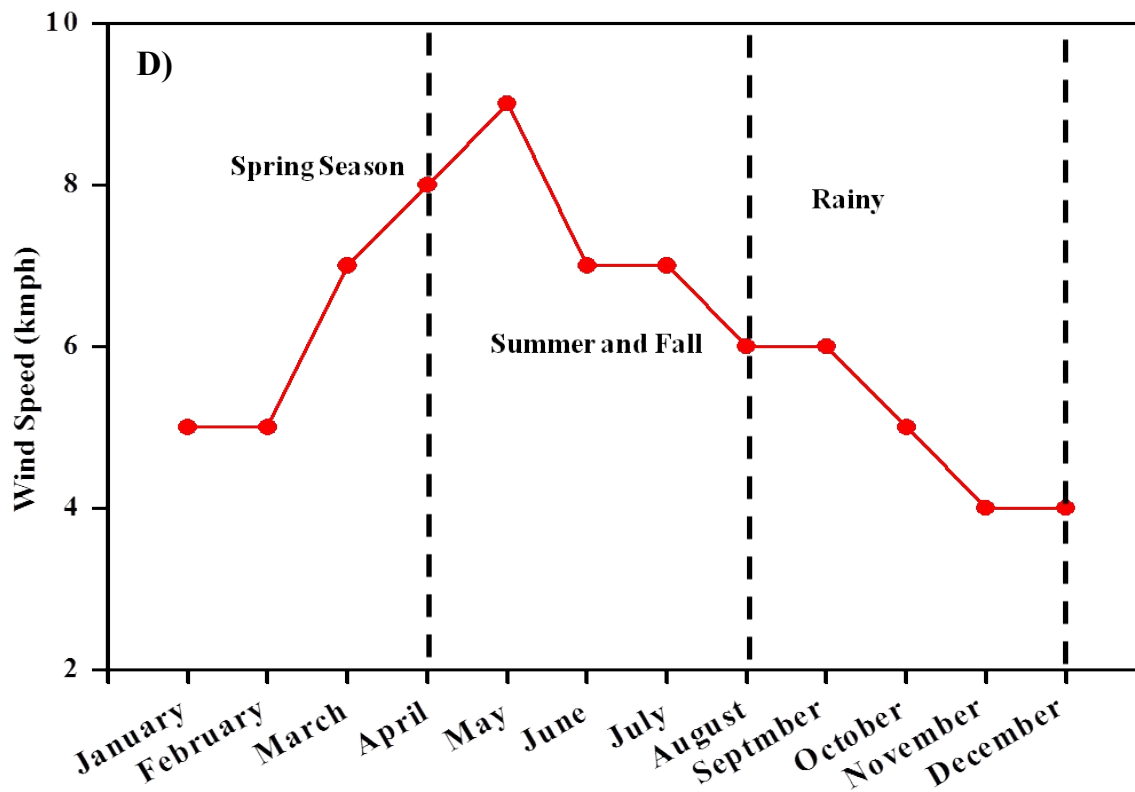


Fig. S3 Photographs of the sulphation plate and wet candle for measuring the Chloride and SO<sub>2</sub> present in the atmospheric environment

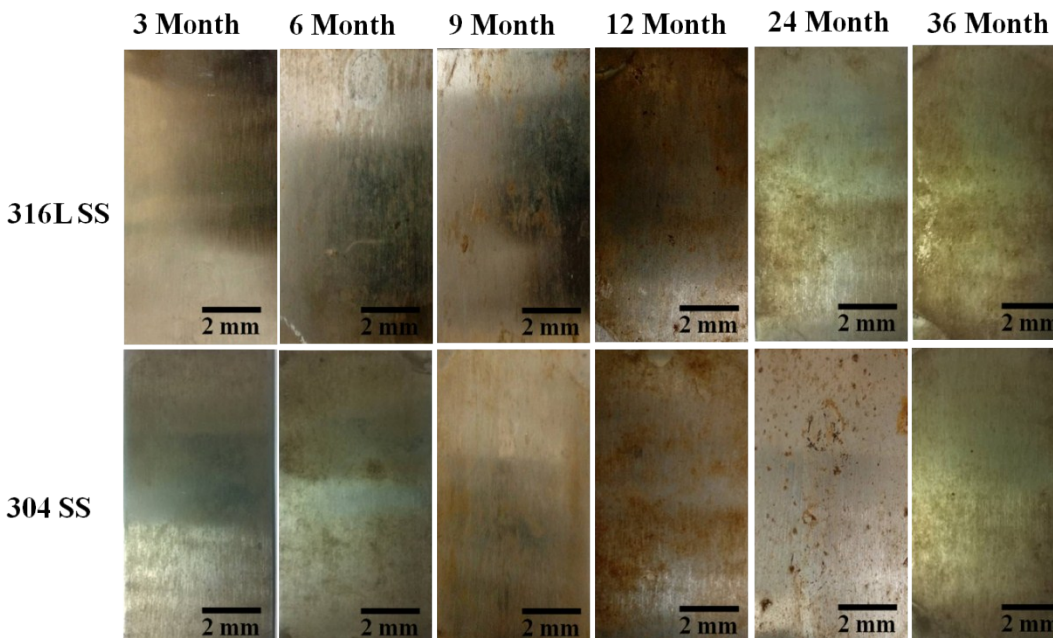




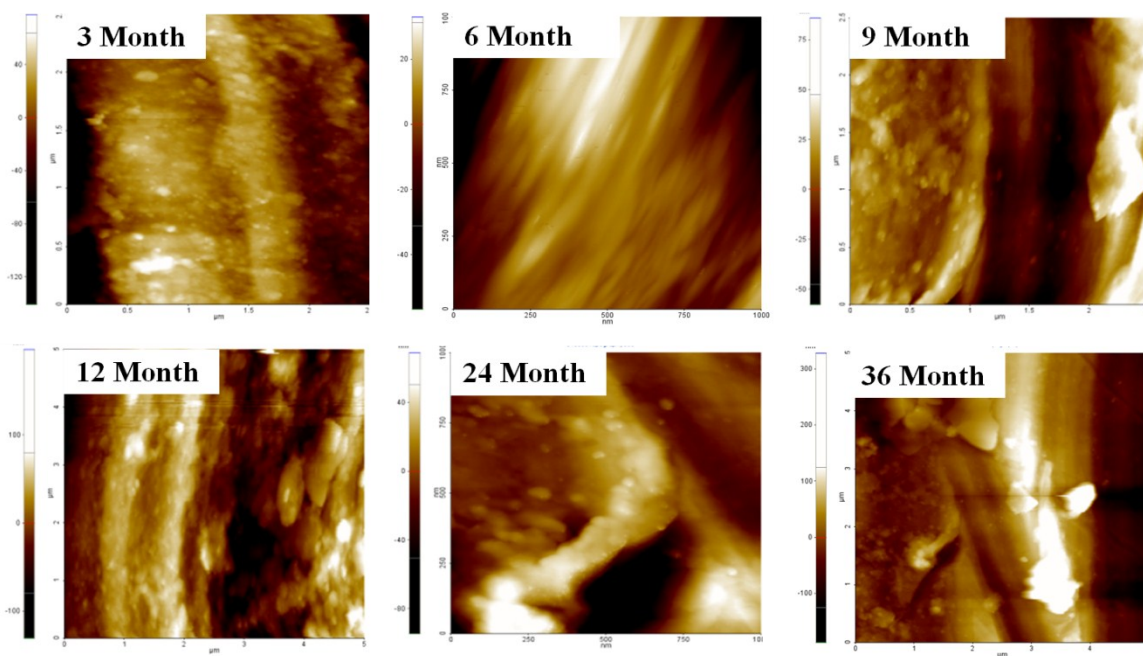




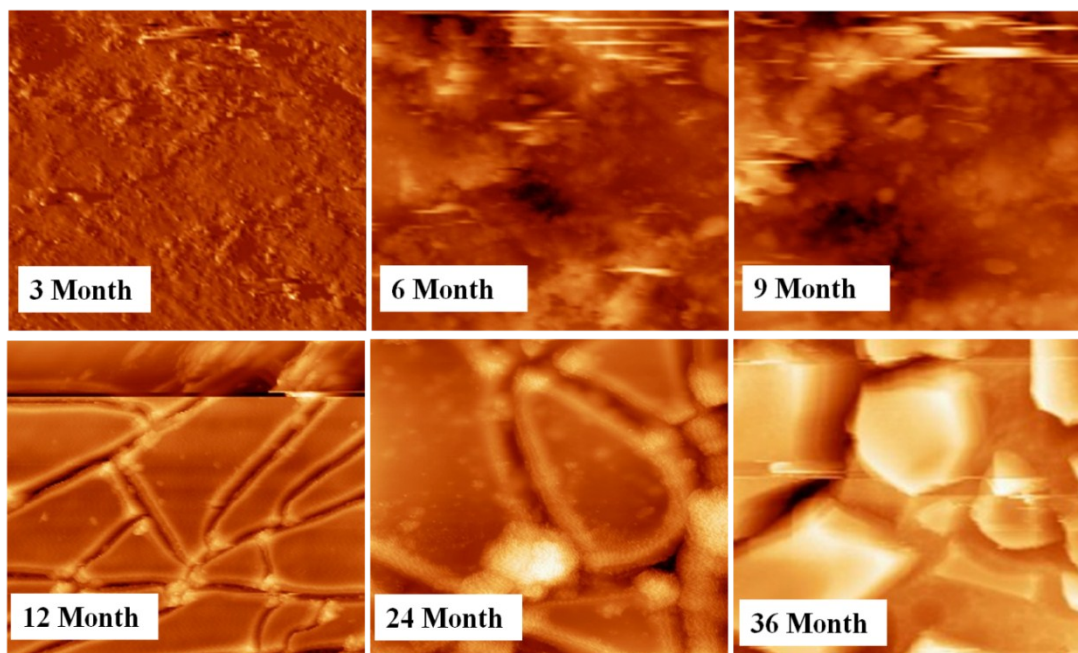
**Fig. S4** Average monthly values of (a) Temperature, (b) relative humidity (RH), (c) rain fall, (d) Wind speed in industrial-marine-urban environment



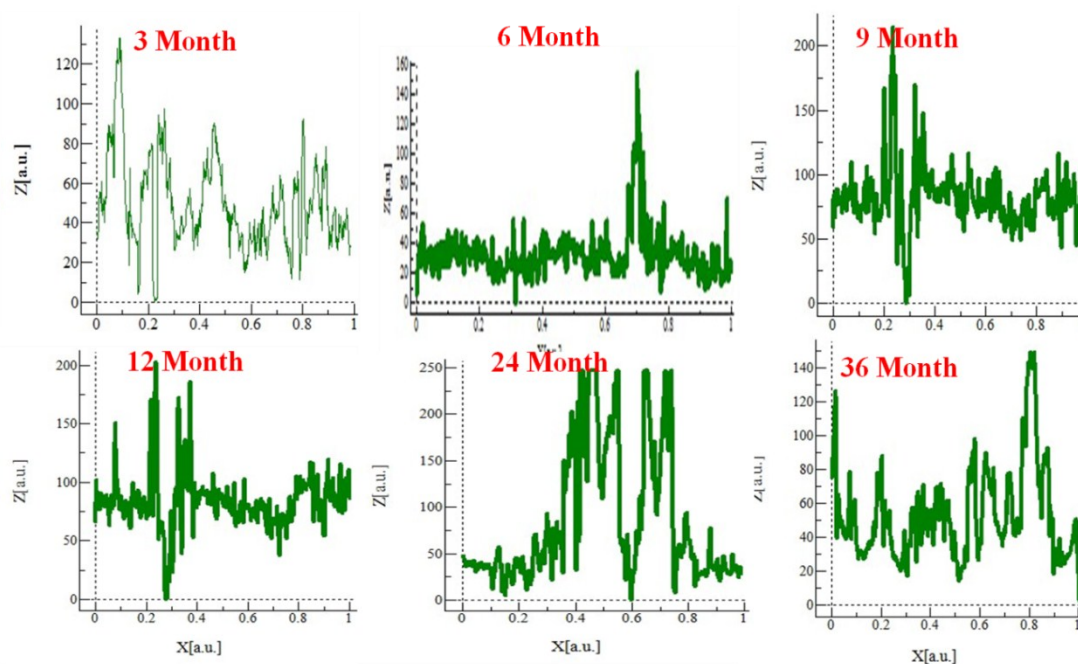
**Fig. S5** Macroscopic images of surface appearance of the 316L and 304 SS specimens exposed for 3 years at industrial-marine-urban environment



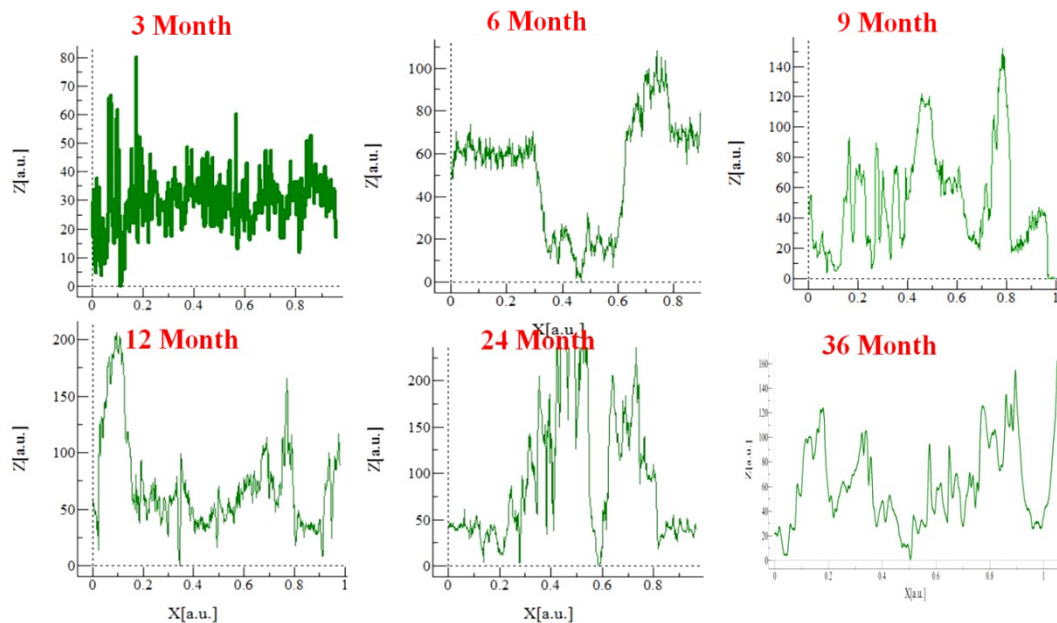
**Fig. S6** AFM images of 316L SS after atmospheric exposure in IMU environment for different durations Chennai



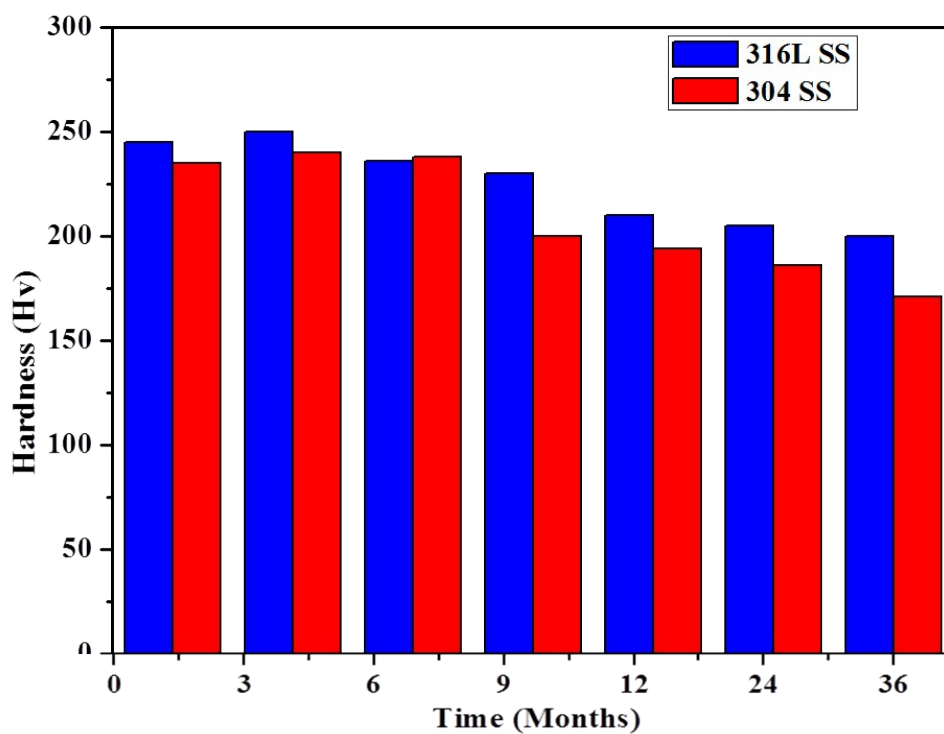
**Fig. S7** AFM images of 304 SS after atmospheric exposure in IMU environment as a function of exposure durations Chennai



**Fig. S8** 2D line analysis SEM images of 316L SS after atmospheric exposure in IMU environment for different durations Chennai



**Fig. S9** 2D line analyses of SEM images of 304 SS after atmospheric exposure in IMU environment for different durations Chennai



**Fig. S10** Hardness of atmospheric corroded 316L and 304 SS for different durations

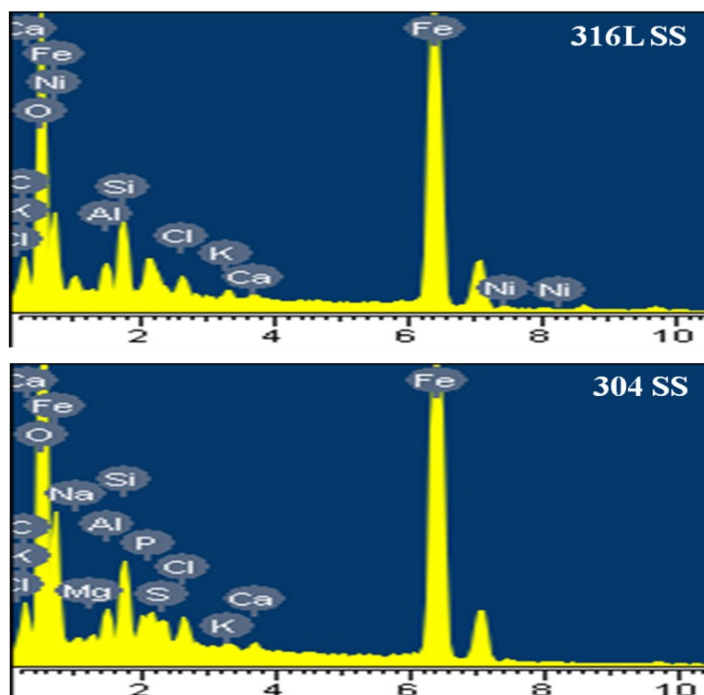


Fig. S11 EDAX spectra of 316L and 304 SS after 3 years of IMU atmospheric corrosion exposure

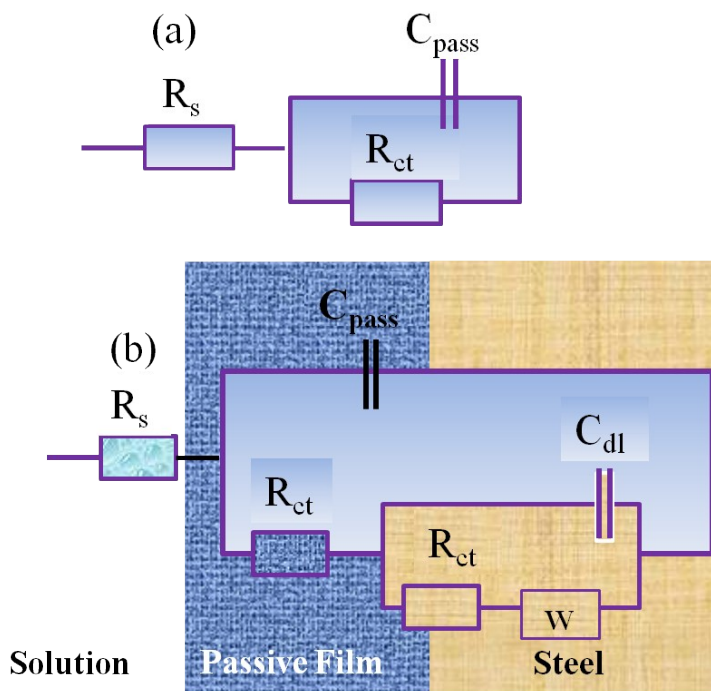
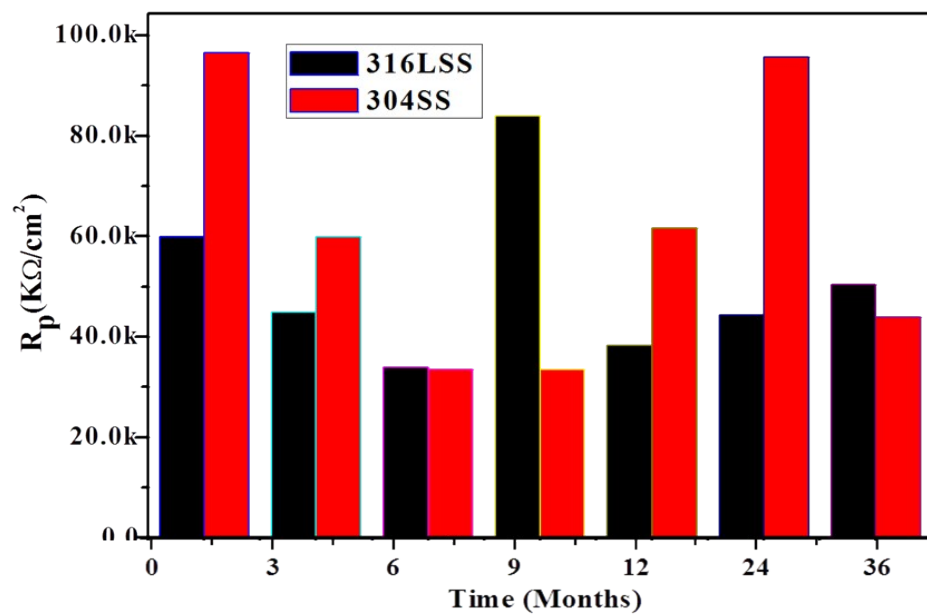


Fig. S12 Equivalent circuits for fitting the EIS data, (a) for bare SS, (b) for atmospheric corrosion exposed in IMU environment



**Fig. S13** Polarization resistance (EIS) behaviour of atmospheric corrosion exposed samples for 3 years in IMU environment Chennai

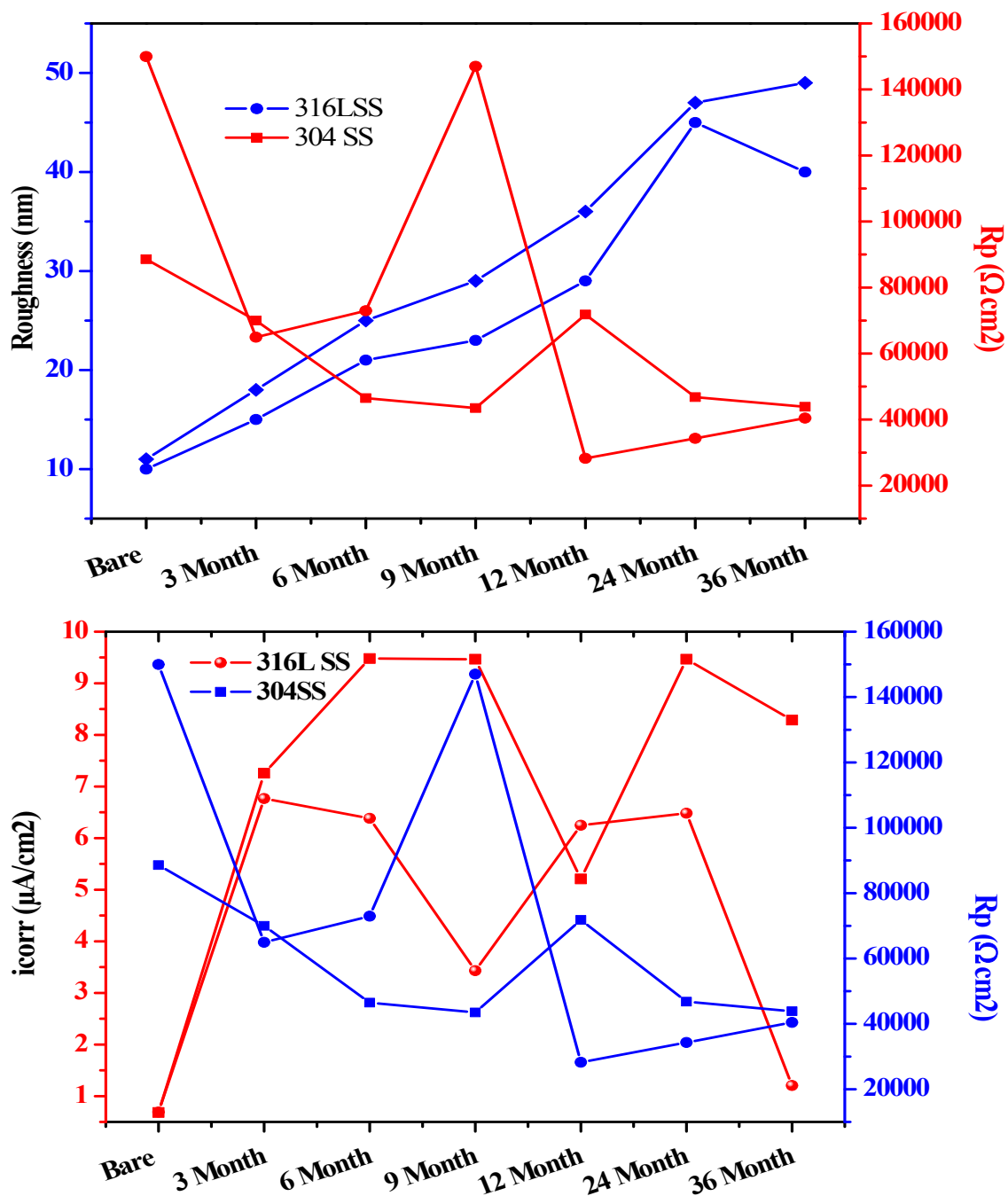


Fig. S14 Comparison of polarization resistance of 316L and 304 SS atmospheric corrosion exposed in IMU environment for 3 years Chennai



**Table S1 Summary of characteristic signature of Raman spectra from the atmospheric exposed stainless steels**

<b>Period of exposure (Months)</b>	<b>Raman signatures 316L SS (cm<sup>-1</sup>)</b>	<b>Raman signatures 304 SS (cm<sup>-1</sup>)</b>
<b>3</b> April-June 2012 (Summer season)	250 Lepidocrocite 300 Goethite 400 Goethite 610 Iron oxide	220 Iron oxide 300 Goethite 400 Goethite 500 Iron oxide 610 Iron oxide
<b>6</b> July-Sept (season) 2012 (Rainy)	220 Iron oxide 300 Goethite 400 Goethite 500 Iron oxide 600 Iron oxide	180 Maghemite 240 Lepidocrocite 300 Goethite 400 Goethite 500 Iron oxide
<b>9</b> Oct-Dec (winter season) 2012	200 Iron oxide 290 Iron oxide 390 Goethite 590 Iron oxide	220 Iron oxide 300 Goethite 400 Goethite 500 Iron oxide 600 Iron oxide
<b>12</b> Jan-March 2013	220 Iron oxide 280 Iron oxide 390 Goethite 500 Iron oxide 600 Iron oxide	190 Iron oxide 220 Iron oxide 300 Goethite 400 Goethite 490 Iron oxide 600 Iron oxide
<b>24</b> April – March 2013-14	270 Maghemite 300 Goethite 390 Goethite 500 Iron oxide 600 Hematite 780 Iron oxide	220 Iron oxide 300 Goethite 400 Goethite 490 Iron oxide 600 Iron oxide
<b>36</b> April- March 2014-15	210 Iron oxide 300 Goethite 400 Goethite 500 Iron oxide 600 Iron oxide	670 Akaganeite 220 Iron oxide 300 Goethite 400 Goethite 500 Iron oxide 600 Iron oxide

### 3. Supporting Information References

1. ASTM G 140-02 2002, 'Standard test method for determining atmospheric chloride deposition rate by wet candle method', ASTM, vol. 11.02, pp. 1-4.
2. ASTM G 91-97 1997, Standard practice for monitoring atmospheric SO<sub>2</sub> using the sulfation plate technique', vol. 11.01, pp. 1-5.
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