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SOIL ZINC CONTAMINATION FROM CORROSION OF GALVANIZED STRUCTURES

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The present work relates to galvanized structures with several years of time life subjected to atmospheric corrosion, like galvanized high tension steel pylons. The mass and fate of zinc released is evaluated both via empirical and experimental procedures. The corrosion rate determination requested atmospheric condition characterization, especially for SO_2 concentration and experimental activities focused on soil sampling around pylons. The soil zinc content, total and exchangeable, is determinates by different analytical procedures. The zinc diffusion in environment and the zinc extension under the top soil is evaluated using 1-dimensional mathematical model for miscible species in porous soil.

Keywords: Atmospheric corrosion; Galvanized structures; Zinc risk assessment; DGT diffusive sampler

1   INTRODUCTION

Recently, great interest has been paid to the risk assessment analysis for manufactured products, containing heavy metals, during their life cycle (Council Regulation EEC 793/93; Kantonales Amt fûr Umweltschutz, 2000; 2001; Smolders *et al.*, 2001). This procedure consists in a complex and multidisciplinary exercise requiring a great amount of environmental data. Presently, only limited and incomplete information on zinc releases for atmospheric corrosion of galvanized structures is available and there is also scarceness on the zinc contamination effects on soil microbial processes. Moreover, chemical analysis protocol in soil aggregates is always a challenging problem, when facing with trace heavy metals.

   In this aspect, the present work looks at the environmental fate of zinc coming from existing galvanized structures exposed to atmospheric corrosion, focusing on zinc release evaluation and propagation into the soil matrix.

   The strategy followed for the study can be synthesized in few major points:

1. Selection of the area where metallic structures are located. The choice is principally based on the possibility to have at the same time meteorological data and pollutant atmospheric levels of the area;

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2. Prevision of metal loss for structures subjected to atmospheric corrosion. At the scope, two empirical methods, the run-off formula (Van Assche, 2000) and the ISO 9223 (1992) are available;
3. Soil sampling activities, mostly addressed at the pylon base, for the analytical determinations of the soil zinc content. Different extraction methodologies where applied (SMT4-CT96-2066; D. M. 11/05/1992; Davison *et al.*, 2000; Zhang *et al.*, 2001);
4. Horizontal and vertical soil zinc distribution, with the aim to represent the migrating scenario. The mathematical model selected is useful for evaluate the propagation of water soluble species through porous media (U.S. EPA, 1986).

2   SELECTION OF AREA UNDER INVESTIGATION

Corrosion depends on the atmospheric environment where the metallic structures are located. Zinc, as most of the heavy metals, becomes more soluble and hence mobile and biologically available with decrement of soil pH. Atmospheric pollution due to emissions of oxidised sulphur, nitrogen compounds and ozone produce acidic substances responsible of the acid wet and dry deposition. The soil acidity increment produces, as consequence, an higher zinc solubility and corrosion velocity over galvanized metallic structures.

The attention to the local climate and pollution characterization of the site under investigation is hence necessary.

The selected pylons are located in a natural valley of the Marche Region (Italy) and they are a part of a high tension line installed since 1971, perpendicularly disposed to the Adriatic sea cost with an overall length of 21 km. The foremost pylon records are summarized in Table I. Two of the three pylons (P58, P60) are located in a rural area with the soil at the base uncultivated and undisturbed. The third pylon (P292) is chosen in an urban area near to an oil refinery, with the aim to examine the influence of more aggressive atmospheric conditions. About meteorological and atmospheric conditions at which all the three pylons are subjected, almost 20 years of weather data have been analysed to characterizes the natural valley microclimatic conditions. The available data are taken from both: the "Osservatorio Geofisico Sperimentale, Sezione di Meteorologia e Climatologia Macerata (Italy)" and the "Servizio Meteorologico dell'Aeronautica Militare Italiana, Stazione Meteorologica di Falconara Marittima (Italy)".

Due to the proximity to the Adriatic sea, the climate is typical littoral (Tab. II), wind velocities and directions indicate mostly North–East breeze conditions. A North–West direction is also present from October to March, when the relative humidity of the area is greater than 70%. Daily SO_2 averaged concentrations, observed during the last ten years, give a mean value of 18.5 $\mu g/m^3$ (Tab. II) with the higher values associated to the North–West direction. Therefore, this direction must be considered as a preferred direction of corrosion for the

TABLE I   Pylon Records.

Pylon data	P58	P60	P292
Life time [years]	30	30	30
Location area	Rural	Rural	Urban/industrial
High [m]	17	17	23
Basal area [m^2]	13	13	18
Weight [kg]	2500	2500	3100
Galvanized surface [m^2]	117	117	136

TABLE II Microclimate Statistics and Pollution Levels.

Microclimate	Pollution levels
Rain: average* per year [mm]	~ 800
Rain: average* per event [mm]	~ 50
Climate	Littoral
Temperature [°C]	$5-25 \pm 7$
Relative humidity range [%]	$70-80 \pm 10$
Wind velocity [m/s]	$3-5 \pm 1.5$
Average# concentration SO_2 [μg/m³]	18.5 ± 10
Average# concentration NO_2 [μg/m³]	38 ± 10
Average# concentration O_3 [μg/m³]	32 ± 10

*Data from 1964 to 1990.
#Data from 1990 to 1999.

selected metallic structure. The air acidity loads, calculated from the observed NO_2, SO_2 and O_3 atmospheric levels (Tab. II), give a contribution to the soil acidity that is lower than the critical value indicated in the reference map for Marche Region (250 eq $H^+ \cdot ha^{-1} \cdot yr^{-1}$ against 1500 eq $H^+ \cdot ha^{-1} \cdot yr^{-1}$) reported in literature (Bonanni *et al.*, 1999). This occurrence must be regarded referring to the contribution to the soil zinc solubility and mobility.

3 ZINC CORROSION PREVISION

Zinc coating corrosion is feasible referring to the procedures described on Table III. The run-off corrosion formula is (Van Assche, 2000):

$$\text{run-off}(g/m^2/yr) = 1.36 + 0.16[SO_2]$$

where SO_2 concentration is the daily mean value of $18.5\,\mu g/m^3$ (Tab. II). Subsequently, the amount of zinc corroded in 30 years of time life is obtained using the structure galvanized surface (Tab. I) and assuming a volume of soil confined around the pylon (see next section). The same methodology has been used for the zinc coating corrosion with ISO 9223.

The corroded zinc amount evaluated with ISO 9223 (1992) and run-off formula match quite well, especially taking into account the more aggressive environment condition around the 292 pylon than the 58 and 60 pylons. The greater zinc concentration estimated for pylon 292 is in accord with the selected corrosion class C_3.

These values have also been compared with the residual galvanized coating thickness, directly measured on the structures (Tab. III). In this case, the corroded zinc is deduced from the difference (Δ) between the initial and the residual structure coating thickness after 30 years of time life. Also in this case the obtained values are in good accord with

TABLE III Zinc Corrosion Evaluation.

	Zn concentration [mg/kg]		
Evaluation method	P58	P60	P292
Corrosion class	C_2	C_2	C_3
ISO 9223	190–1350	190–1350	1240–3820
Run-off	1150	1150	1390
Δ Thickness	1230	1230	1460

that predicted by the theoretical models, suggesting an amount of zinc expected in soil included in these ranges. The most cautious mass of zinc released from the existing structures will be used for the successive environmental dispersion evaluation.

4 EXPERIMENTAL ACTIVITIES

The zinc soil amount has been evaluated excavating soil samples in proximity of the pylons in correspondence of the feet and the centre. Soil samples have also been taken in North–West direction up to a distance of 50 m from the support base and up to 2 m in South–West direction following the scheme reported in Figure 1. Sampling has been carried out with a steel cylinder (8 cm of diameter), manually introduced down to the depth of 45 cm. Higher depths, when necessary, have been obtained realizing a preliminary hole of 50 cm. After slicing (in single slice of 15 cm, each one signed with A, B and C), drying (in oven at 40 °C), sieving (at 0.2 mm) and homogenisation procedures, the analytical determinations on the remoulded soils have been carried out.

Soil metal extraction procedure is one of the most important aspects to be considered since the necessity of a comparison of the observed concentrations with the legal standards values. Zinc extraction is carried out following the recent report of the leaching extraction tests (SMT4-CT96-2066). The procedure requires sequential extractions with solutions at different leaching strength. In fact, they simulate different soil conditions like: salinity, cation exchange canal:concentration, presence of organic substances and presence of complexating agents. Total zinc concentration is determinate, instead, by soil mineralization in mineral acid (D. M. 11/05/1992).

Conventional methods of measuring trace heavy metals in soil solution, based on chemical extractions, are compared with a new method based on diffusive gradients in thin films (DGT) device. This technique accumulates metals on a resin layer after diffusive transport
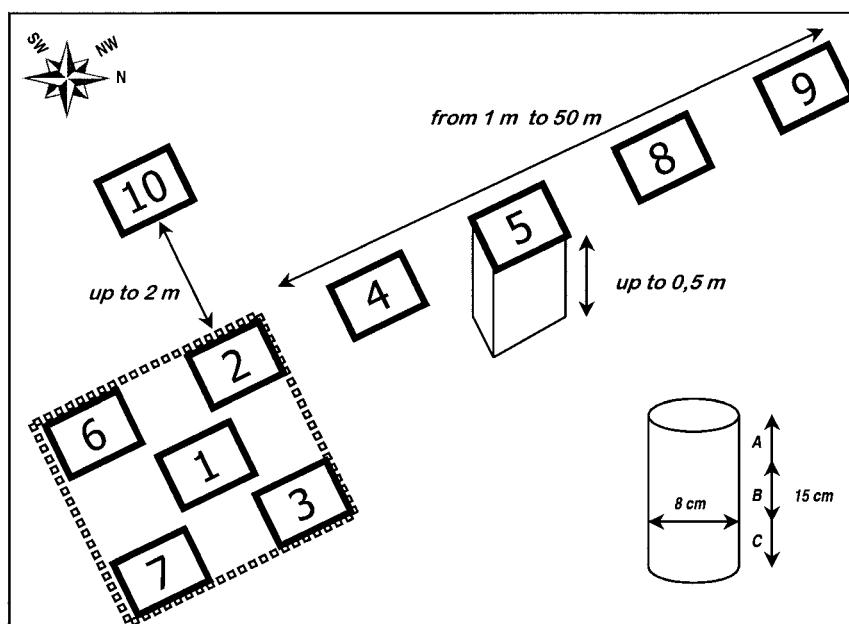
FIGURE 1 Soil sampling scheme and sample number.

through a diffusive gel (Zhang *et al.*, 2001). The major advantage of DGT device is that it gives the possibility to obtain the exchangeable metal at the natural soil pH and it can be used directly in water and sediment. However, in presence of natural soil at low water content the *in situ* use could be limited.

The procedure followed for the metal extraction is taken from Davison *et al.* (2000). Considering the water content conditions of the natural soil ($10 < w[\%] < 30$), the device has been used in laboratory on remoulded samples adding 80% of water to the dry soil. The obtained soil samples are stored in a humidity controlled wet room and leaved in contact with the sampler for several days for the diffusion process realisation.

5 SOIL ZINC ANALYSES

Diffractometric determinations on soil in correspondence of each pylon have been performed to characterize clay fraction and type of minerals. The X-ray diffractograms obtained furnish an acceptable homogeneity in soil composition. The dominant minerals observed were silicates, calcite and alum-silicates. In agreement with the measured soil pH, always higher than 7 (from 7 to 9), zinc hydroxide have been observed for the samples with higher zinc content (see Tab. IV), only in some most superficial samples, zinc carbonate hydrated was distinguishable.

The average total zinc concentration measured is reported in Table IVa and IVb. As evident from these results, the soil volume interested to zinc propagation is really quite circumscribed. At a distance greater than 50 cm from the pylon feet and depth higher than 50 cm, the zinc concentration equals everywhere the background level. The overall set of results obtained parallel values reported in literature (Kantonales Amt fûr Umweltschutz, 2000; 2001; Smolders *et al.*, 2001) for similar conditions. Values less than 33 mg/kg indicate zinc concentrations equal to those of the local soil background. However, in correspondence of the structure some values exceeded the reference levels admitted by some European legislation (RS 814.12). In any case, as far as risk assessment evaluation is concerned, the zinc soil screening level (SSL) does not appear to be exceeded (U.S. EPA, 1994).

As expected, the exchangeable zinc gives values strongly dependent to leaching conditions (Tab. V). The exchangeable zinc obtained with DGT method in 58 pylon equal the leaching extraction with $CaCl_2$. Anyway, further work is in progress to increase the confidence in this observation.

6 SOIL ZINC DISPERSION

The measured versus predicted total zinc concentration, as referred to the dry soil volume under the pylon, match quite well: the balance between the calculated corrosion with ISO 9223 and that effectively measured prompt for a zinc localisation exclusively under the galvanised pylon structure (Tab. VI). The environmental propagation has been possibly limited by the specific characteristics of the soil itself (particularly referring to soil pH and clay minerals) and by the low incidence of acid rains previously discussed.

This aspect is drowed in Figure 2, where total zinc concentrations, normalized respect to the maximum zinc concentration, is plotted as horizontal distribution. In all tree pylons, the total amount of zinc released is found just around the pylon itself: 1 m is the maximum distance where significant values, different from the background, could be measured. The profiles are compared with some results reported in literature, where zinc dispersion occurs to a greater distance, with significant values observed up to 10 m (Smolders *et al.*, 2001).

TABLE IVa Total Zinc Concentrations [mg/kg] Under the Pylon Base with Depth.

	Sample #1			#6			#2			#3			#7		
	P58	P60	P292	P58	P60	P292	P58	P60	P292	P58	P60	P292	P58	P60	P292
A – 15 cm	806	1442	1784	–	266	–	1486	3743	7932	350	508	–	–	295	3121
B – 30 cm	336	178	442	–	<33	–	645	2853	5900	<33	815	–	–	518	360
C – 45 cm	<33	96	1198	–	751	–	<33	274	1267	<33	156	–	–	857	1292
D – 100 cm	<33	<33	<33	–	<33	–	<33	<33	<33	<33	<33	–	–	<33	<33

TABLE IVb Total Zinc Concentrations [mg/kg] of Sample Number (#), Distances [m] and Direction from the Pylon Feet with Depth.

	#10: 2 m – SW			#4: 0.5 m – NW			#5: 1 m – NW			#8: 10 m – NW			#9: 50 m – NW		
	P58	P60	P292	P58	P60	P292	P58	P60	P292	P58	P60	P292	P58	P60	P292
A – 15 cm	–	–	122	<33	<33	628	<33	<33	<33	<33	<33	<33	<33	<33	<33
B – 30 cm	–	–	<33	<33	<33	63	<33	<33	<33	<33	<33	<33	<33	<33	<33
C – 45 cm	–	–	<33	<33	<33	42	<33	<33	<33	<33	<33	<33	<33	<33	<33
D – 100 cm	–	–	<33	<33	<33	<33	<33	<33	<33	<33	<33	<33	<33	<33	<33

TABLE V   Exchangeable Zinc [mg/kg] in Soil Samples.

Extraction method		Zn concentration [mg/kg]		
		P58	P60	P292
NaNO$_3$	A	7.9	<0.5	7.8
	B	<0.5	14.6	3.1
	C	<0.5	<0.5	<0.5
CaCl$_2$	A	34.2	203.3	28.9
	B	4.7	88.6	4.5
	C	1.8	3.2	3.2
CH$_3$COOH/Na	A	37.9	220.2	34.4
	B	6.8	94.6	5.8
	C	6.4	5.2	5.9
EDTA	A	454.2	756.8	516.4
	B	148.8	532.7	26.9
	C	7.2	47.3	174.8
DGT – pylon P58		*24h**	*48h**	*96h**
	A	13	22.3	27.5

*Contact time DGT – soil.

To describe the vertical distribution of the corroded zinc under the pylon base a propagation model, concerning advection/diffusion processes for soluble chemical species in porous media, is selected with the analytical solution furnished by (U.S. EPA, 1986):

$$\frac{c}{c_0} = \frac{1}{2}\left[\text{erf}\left(\frac{R \cdot (x + x_0) - v \cdot t}{2\sqrt{D \cdot R \cdot t}}\right) - \text{erf}\left(\frac{R \cdot x - v \cdot t}{2\sqrt{D \cdot R \cdot t}}\right)\right] \qquad (1)$$

where c (M/L^3) is the concentration in liquid phase; x_0 (L) is the source contamination depth at initial concentration c_0, D (L^2/T) is the zinc diffusion coefficient into the soil water, $R(-)$ is the retardation factor, t is the time (T) and x the space (L). The retardation factor (R) linearly depends to the distribution coefficient, k_d (L^3/M), of zinc between solid and liquid phases into the soil. The model reproduces typical boundary conditions of zinc migration in soil; no chemical/biological decay and the following initials conditions is possible to assume:

(1) the zinc ion concentration, c_0, available to the transport is in equilibrium with pH typical of rain (pH ~ 6.5), *i.e.* $c_0 \sim 590$ mg/kg;
(2) the depth of the contamination source, x_0, is a function of the height average of rain per event (Tab. II) and soil total porosity ($n = 0.5$), *i.e.* $x_0 \sim 100$ mm.
(3) the effective velocity, v, depends on grain size distribution, clay fraction content, saturation degree and natural water content, *i.e.* $v = 1 \times 10^{-9}$ m/s.

The vertical profiles are obtained using different distribution coefficients values to refer to the zinc mobility in soil. In the first graph (Fig. 3a), diffusion coefficient and k_d values are obtained interpolating with Eq. (1) the experimental data; in particular, a low k_d (3.5 ml/g)

TABLE VI   Zinc Mass Balance.

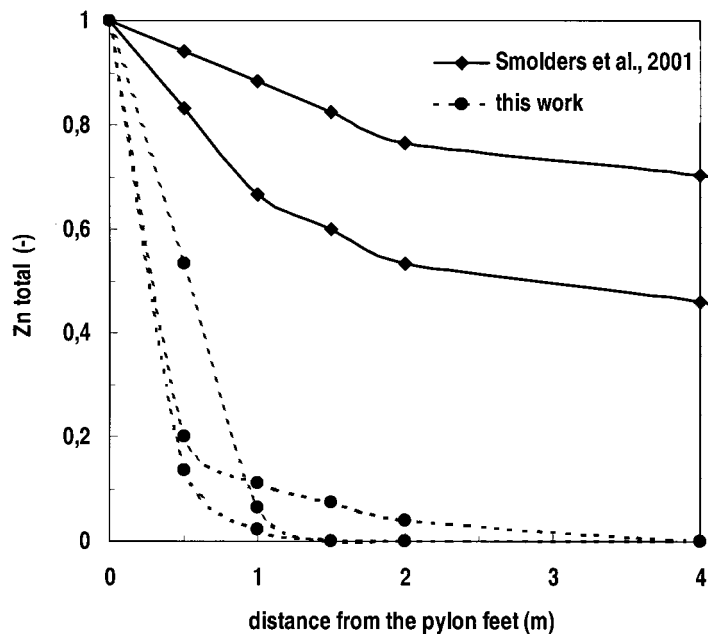| Evaluation method	Zn concentration [mg/kg]		
	P58	P60	P292
Corrosion class	C_2	C_2	C_3
ISO 9223	190–1350	190–1350	1240–3820
Experimental soil analysis	350	767	2541

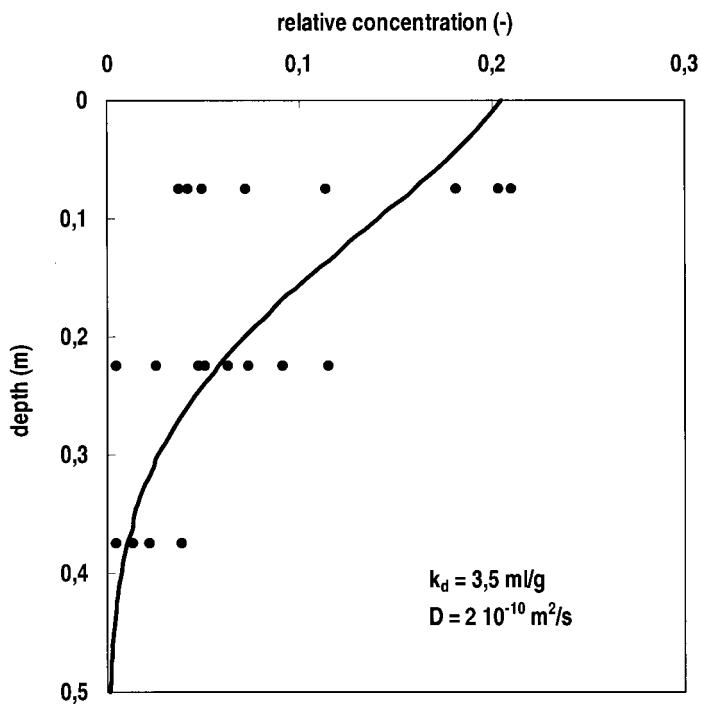FIGURE 2   Horizontal distribution of zinc in soil.

FIGURE 3a   Vertical distribution of zinc in soil: parameters from experimental data interpolation.
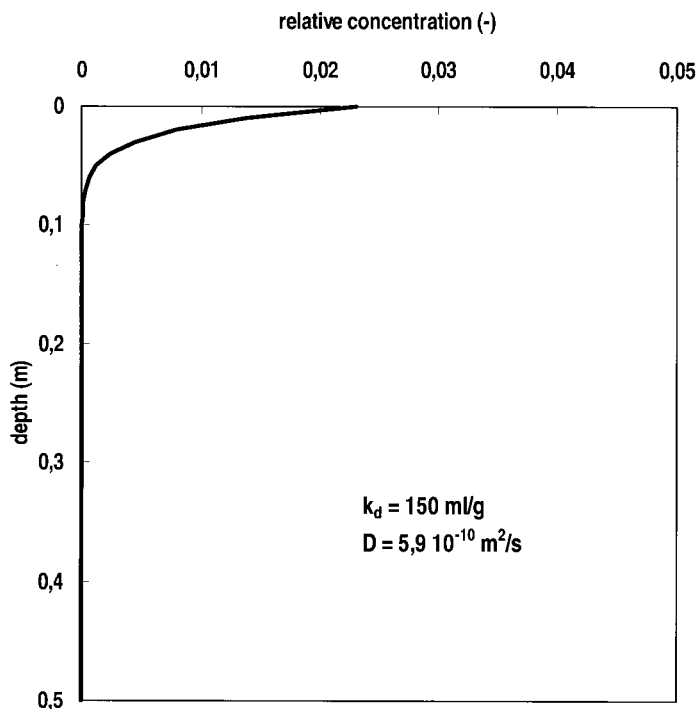
FIGURE 3b   Vertical distribution of zinc in soil: parameters from Ermstberger *et al.* (2002).

is obtained. In the second graph (Fig. 3b) a simulated concentration profile is reported without modifying the initial and boundary conditions and using k_d and D parameters as reported by Ermstberger *et al.* (2002). As recognizable by the graphs, the zinc diffusion coefficient (D) obtained are quite comparable, in particular referring to the differences in terms of distribution coefficient (k_d). The diffusion coefficient influences less the zinc profile shape in soil than k_d parameter, which differs more than one order of magnitude. The observed differences in k_d values can be possibly attributed to different environmental and leaching conditions performing exchangeable zinc procedures. However, the soil volume interested from the migration is quite comparable in both cases (10–20 cm versus 50 cm).

7   CONCLUSION

We can summarize the results of the research in these few conclusive points:

1. The empirical formulations for zinc corrosion calculation appear in the first instance in good agreement with experimental results.
2. The released zinc by atmospheric corrosion is confined under the structure base itself. The polluted volume estimated has a depth of approximately 50 cm and distance from the basal area of the pylon of approximately 50 cm.
3. With reference to the standard legal values, the zinc concentration measured in this volume of soil are sometimes higher than the reference limits.
4. The specificity of the selected sites guarantees low mobility to the metal corroded from galvanized structure.

Finally, it would be interesting to extend the experimental framework to soils with lower neutralising capacity and to higher atmospheric pollution levels different from those examined.

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