Environmental Monitoring and Assessment (2017) 189:523
DOI 10.1007/s10661-017-6240-8

Effects of middle term land reclamation on Nickel soil-water interaction: a case study from reclaimed salt marshes of Po River Delta, Italy

Dario Di Giuseppe[a1], Massimiliano Melchiorre[b2*], Barbara Faccini[3], Giacomo Ferretti[3], Massimo Coltorti[3]

[1] DISTABIF, Department of Environmental, Biological and Pharmaceutical Sciences and Technologies, Second University of Naples. Via Vivaldi 43, 81100 Caserta, Italy

[2] Group of Dynamics of the Lithosphere, Institute of Earth Sciences Jaume Almera ICTJA – CSIC, Lluís Solé i Sabarís s/n, 08028 Barcelona, Spain;

[3] Physics and Earth Science Department, University of Ferrara. Via Saragat 1, 44122 Ferrara, Italy;

*Corresponding Author: Massimiliano Melchiorre[b]. E-mail address: mmelchiorre@ictja.csic.es

[a] Dario Di Giuseppe[1] **ORCID: 0000-0003-1726-4531**

[b] Massimiliano Melchiorre[2] **ORCID: 0000-0002-6212-4661**

Abstract

Reclaimed salt marshes are fragile environments where water salinization and accumulation of heavy metals can easily occur. This type of environment constitutes a large part of the Po River Delta (Italy), where intensive agricultural activities take place. Given the higher Ni background of Po River Delta soils and its natural water-soluble characteristic, the main aim of this contribution is to understand if reclamation can influence the Ni behavior over time.

In this study, we investigated the geochemical features of 40 soils sampled in two different localities from the Po River Delta with different reclamation ages. Samples of salt marsh soils reclaimed in 1964 were taken from Valle del Mezzano while soils reclaimed in 1872 were taken nearby Codigoro town. Batch solubility tests and consecutive determination of Ni in pore-water were compared to bulk physicochemical compositions of soils.

Bulk Ni content of the studied soils is naturally high, since these soils originated from Po River sediments derived from the erosion of ultramafic rocks. Moreover, it seems that Ni concentration increases during soil evolution, being probably related to the degradation of serpentine. Instead, the water soluble Ni measured in the leaching tests is greater in soils recently reclaimed compared to the oldest soils.

Soil properties of two soil profiles from a reclaimed wetland area were examined to determine soil evolution over one century. Following reclamation, pedogenic processes of the superficial horizons resulted in organic matter mineralization, pH buffer and a decrease of Ni water solubility from recently to evolved reclaimed soil.

Keywords: Ni water solubility, leaching tests, reclaimed wetland, time evolution of soil.

Introduction

The reclamation of salt marsh areas is a common and widespread practice that since the beginning of the history of agriculture has been developed to supply inhabitable lands and cultivable soils (Li et al. 2014). Salt marsh reclaimed soils management has however to take into account problems related to both economic (high needs of power for water pumps) and agricultural (high salinity soils) aspects (Utset and Borroto 2001). The disadvantages of reclamation are mainly related to a series of physical and chemical changes that the soils suffer as well as the release of trace elements and CO_2 in the environment (Fernández et al. 2010). Other drawbacks of this technique are represented by the loss of ecosystems of high biodiversity (Doody 2001) and by the end of salt marsh function as carbon sinks (Connor et al. 2001; Lal 2001).

Po River Delta is situated in the north east part of Italy (Fig. 1) flowing into the Adriatic Sea. This area has been affected since the Roman period by several episodes of reclamation for agricultural purposes. Nowadays these soils are mainly used to cultivate cereals and horticultural crops.

These soils have been widely investigated emphasizing the presence of high natural geochemical anomalies such as Ni and Cr related to the presence of serpentine and chlorite minerals reflecting the drainage of the Po River from the ophiolitic complexes of the western Alps and north western Apennines (Amorosi et al. 2002; Bianchini et al. 2002; Amorosi and Sammartino 2007; Dinelli et al. 2007; Amorosi 2012; Bianchini et al. 2012; Amorosi et al. 2014, Di Giuseppe et al. 2014a, Di Giuseppe et al. 2016, Melchiorre et al. 2016). Ni content from alluvial sediments in Po River Delta no-reclaimed soils displays a moderate mobility related to the metastable behavior of serpentine (Bianchini et al. 2013a). Furthermore, Ni is water-soluble and should be monitored to avoid its possible transfer in the water bodies and bioaccumulation in the food chain (Bianchini et al., 2013a).

Therefore, given the higher Ni background of Po River Delta soils and its natural water-soluble characteristic, the main aim of this contribution is to understand if reclamation can influence the Ni behavior over time. .

Outcomes of this study can help to understand if among the various processes that characterize the time soil evolution of reclaimed salt marsh there is also the serpentine degradation and the consequent Ni availability.

Material and methods

Study areas

Since its formation about 3,000 years ago, the area of the Po River Delta (belonging to the UNESCO World Heritage List) has played a fundamental role in the development of civilization. The evolution of the hydrographic network of the river from the late Bronze Age until today, created a delta that extends for more than 730 km^2, hosting one of the most important Italian agricultural areas (Stefani and Vincenzi 2005). The geological setting of the Delta Plain is dominated by the Po River and by its ancient and present alluvial and delta deposits. Sediments occupy an area extending from the city of Ferrara to the Adriatic Sea coast. Within the delta system, it can be possible to distinguish the coarse deposits (gravel and sand) of the interdistributary channels and their banks, and the fine deposits (silt, clay and peat) of brackish marsh and interdistributary bays (Fig. 2 top).

Valle del Mezzano (hereafter VM) is a wide depressed area (currently few meters below sea level) of 190 km^2 belonging to the eastern Province of Ferrara (Emilia Romagna, Italy) and situated in the southeastern part of the Delta. This area has been recently reclaimed (1960s) with electric water pump. Soils sampled in this area are fine-grained and particularly enriched of organic matter (Terric Sulfisaprist, Thionic Histosols, IUSS-WRB 2007). Histosols are the most representative soils, coupled with subordinate Histic Humaquests. pH ranges from neutral to sub-acid in surface layers (7.7-6.0) and from sub-acid to acid in the deeper horizons (6.5-5.2). The high salinity is reflected in high Electric Conductivity (EC) values ranging from 0.7 to 5.8 mS/cm in the A horizon and from 1.2 to 13.5 mS/cm in the B horizon. The description of profiles representative of these soil units (taken from the web site of the Emilia Romagna Region, www.suolo.it) is reported in Di Giuseppe et al. (2014b).

Soils sampled nearby Codigoro town (Fig.1) come from an extended agricultural area reclaimed during the XIX century using steam engines (Fig. 2). The soils are classified as Humi Thionic Fluvisols Thapthohistic according to the World Reference Base (WRB) classification (IUSS-WRB 2007). On average, the texture is silty clay in the upper layers (Oe and Ap) and clayey silt in the lower layer (Cg) of the profile. The pH ranges from 6.3 to 7.6 in the Ap horizons; it decreases in the organic Oe layer (5.8 – 6.9), and varies between 6.1 and 7.4 in the Cg horizon. The soil salinity increases rapidly from Ap (2.0 mS/cm) to Cg (8.0 mS/cm) horizon. Accurate description of soil profile is available in Di Giuseppe et al. (2014c).

Analytical procedure

Forty soils sampled in two different localities from the Po River Delta with different reclamation ages have been investigated (Fig. 1). Samples of salt marsh soils reclaimed in 1964 were taken from VM area and samples of salt wetland reclaimed in 1872 were taken nearby Codigoro town (COD).

The soils sampling was carried out with an Edelman auger (Eijkelkamp) during the summer 2009 for VM and at the end of October 2011 for COD. Following Bianchini et al. (2012) in each sampling site two samples were collected, one representative of the A horizon (topsoil) and the other of the underlying B horizon (subsoil).

Total Ni concentrations of soil samples measured with Wavelength-Dispersive X-ray Fluorescence (WD-XRF; Di Giuseppe et al. 2014a) are collected in the databases published by Di Giuseppe et al. (2014b) and Di Giuseppe et al. (2014c).

The mineralogical characterization was carried out by X-Ray Powder Diffraction (XRPD) analysis following the procedure of Malferrari et al. (2013).

Batch solubility tests were performed using the saturation soil extraction (SSE) methods described by Colombani et al. (2015) in a temperature-controlled laboratory at 20±0.5°C. Sediments were not sterilized but air-dried at room temperature to minimize heat driven dehydration reactions and to avoid changes in the structure, ion exchange capacities and dissolution characteristics of the clay minerals.

Twenty batches were run with a solid:liquid ratio of 1:5 (w/v), using 5 g of air-dried sediment and 25 ml of synthetic rainwater (deionized water plus $CaCl_2$ 0.01 mM and $NaCO_3$ 0.01 mM; pH=7.6) and for each batch, triplicates were prepared to derive standard deviation of concentration. pH and EC were measured using a multiparametric probe in the soil-water solution.

Batches were sealed and placed on a rotary shaker for 1 h at 20°C to achieve equilibrium, prior to collecting samples (2 ml each) to be analyzed for Ni by inductively coupled plasma mass spectrometry (ICP-MS) using a Thermo-Scientific X Series instrument. Known amount of Re and Rh were introduced as internal standard; in each analytical session, the analysis of samples was verified with that of the reference materials EU-L-1 and ES-L1 provided by SCP-Science (www.scpscience.com). No filtration was performed before the analyses in order to provide the real composition of the soil solutions. These are constituted by soluble salts and colloids or several other chemical components that filtration would have altered.

Solid–solution Ni partitioning was evaluated using the ratio of metal concentration in the particulate to liquid phases of soil, i.e. the partition coefficients (K_d; Luo et al. 2006). K_d was defined as the coefficient of partition between soil and water at equilibrium and log K_d values higher than 2.8 represent a low solubility (Vittori Antisari et al. 2013).

The organic matter content (OM), expressed in weight percent and was measured by dry combustion (Tiessen and Moir 1993). The water content was measured gravimetrically in saturated condition after heating the samples for 24 hours at 105°C (Danielson and Sutherland 1986). Percentage of clay content in soil was estimated by wet sieving and by means of a Micromeritics Sedigraph 5100.

Batch solubility tests and consecutive determination of Ni in pore-water were compared to physicochemical compositions of VM and COD soils reported in Di Giuseppe et al. (2014b) and Di Giuseppe et al. (2014c), respectively. Regarding the mineralogical composition of COD and VM soils data were taken from Malferrari et al. (2013) and Di Giuseppe et al. (2014b).

The One Way ANOVA test was performed in order to verify any significant variation in the dataset of the two different sampled areas. The differences between groups of data are significant, only when p value is below 0.5.

Results and discussions

The main pedogenic process affecting the studied soils after drainage resulted in OM mineralization, oxidation and gleying (Bini and Zilocchi 2004).

Comparing the data obtained for VM and COD soils it is possible to observe how the investigated parameters evolved with the reclamation time. OM and EC decrease passing from VM to COD, ranging on average between 18.2% and 8.5 and from 4.3 mS/cm to 1.6 mS/cm respectively. On the other hand pH increases from an average of 6.3 to 7.4 (Table1). According to Saljnikov et al. (2013) OM decomposition may be linked to the crop management systems, such as bad crop rotation and tillage, whereas the salinity decrease is probably related to the percolation of rain and irrigation waters that "wash" and desalinize the superficial horizons (Di Giuseppe et al. 2014c). Variation of pH from weakly acid to weakly alkaline in reclaimed soils is known in literature (e.g. Bini and Zilocchi 2004), but its cause is still not clear. Probably the higher carbonates contents of Po River Delta soils (Di Giuseppe et al. 2014b; Di Giuseppe et al. 2014c) played a certain role in this pH variation.

Total Ni concentrations in the studied soils are shown in Table 1 and Figure 3. On the whole, they are quite higher with respect to the average concentration (32.6 mg/kg) recorded in the Ap soils from other European sites (Albanese et al. 2015). This is interpreted as a natural geogenic anomaly affecting the soils from the eastern province of Ferrara (Bianchini et al. 2013b). This is also supported by the high Ni content of ancient bricks (and mortars) from historical buildings of the Emilia Romagna region (Di Giuseppe et al. 2014a) made with local sediments analogous to those considered in this study and manufactured in times preceding any significant form of anthropogenic pollution.

In Figure 3, Ni concentrations in topsoil A horizon are compared with those of the subsurface B horizon. The first thing leaping out is that average bulk Ni concentration of COD is higher than VM samples ($p<0.1$). VM soils show a surface enrichment of Ni. Even though this anomaly is usually a marker of anthropogenic metals pollutions, in this case it is related to the different grain size of the two horizons. Following Bianchini et al. (2012) in fact, Ni bulk concentration in soils of the Po River Delta is related to the clay content; therefore, because of the higher clay percentage in VM's A horizon than B horizon (Table 1), the Ni superficial enrichment is a natural anomaly. On the other hand, the similar Ni concentration in both COD A and B horizons is due to the analogous clay percentages in the two horizons (Table 1). .

VM soils have average bulk Ni concentrations of 106 mg/kg, while COD soils average concentration is 142 mg/kg. COD Ni concentrations not exceeding the baseline value of Ni for Po River Delta soils (231 mg/kg for the interdistributary area of Po river catchment according to Amorosi et al. 2014) rule out anthropogenic pollution.

Probably the high Ni concentrations in COD soils are due to the prolonged exposure to oxidizing conditions, generating favorable conditions for weathering process. These conditions produced the progressive destabilization in serpentine supergene environment (Bianchini et al. 2013b) and maybe increased the Ni concentration in the soil. A further support to this hypothesis is the XRD analysis performed on VM and COD soil samples. VM samples contain traces of serpentine among the clay minerals (Di Giuseppe et al., 2014b), while Malferrari et al. (2013) analyzed 20 COD superficial samples and never find out serpentine.

Ni concentrations measured in the leaching tests are show in Table 2. VM soils have average Ni values of 251 µg/kg, while for COD Ni average concentration is 43 µg/kg. Table 2 also shows that there are significant differences (<0.1) among the $\log K_d$ values. VM samples have a range of K_d values between $\log K_d$ 2.3 and 4.0, whereas $\log K_d$ COD range from 2.8 to 4.8. It is important to note that among the VM leaching tests, 14 samples out of 20 showed values of $\log K_d$ below the critical value of 2.8.

No correlation was found comparing the obtained $\log K_d$ values with the soils geochemical composition database (Di Giuseppe et al. 2014b; Di Giuseppe et al. 2014c). The only significant correlation ($R^2=0.55$) is the negative one between the Ni soil-water K_d values of VM soils and their OM content (Fig. 4). This would therefore support what already stated by Syrovetnik et al. (2007) which emphasized that peat deposits formed in anaerobic and waterlogged ecosystems are enriched in heavy metals.

The evolution of the Ni concentration in the VM soils is therefore strictly related to two different and consecutive processes. The availability of the Ni is provided by the serpentine weathering as proposed by Bianchini et al. (2013b), while the successive Ni bond with the OM is linked to the OM's retention capacity.

Conclusions

Reclamation of salt marsh causes drastic pedogenic modification. In the Po River Delta, soils were reclaimed in different periods, thus allowing a study of their evolution over time.

Total Ni content of the studied soils is naturally high, since these soils originated from Po river Delta sediments derived from the erosion of ultramafic rocks. Moreover, it seems that Ni concentration increases during soil evolution, being probably related to the degradation of serpentine. High Ni concentration in soils' moistures of VM represents an environmental problem, considering that the observed low soil's pH favors its mobility and it can be transferred to the crops and to the humans, being in some cases very dangerous for human health.

In our study, we compared the soil compositions of two reclaimed areas belonging to the Po River Delta and the results can be summarized as follow:

1. Recently reclaimed salt marshes (i.e. those from VM) of the Po River Delta are characterized by high salinity and high organic matter contents. Comparing these soils with those from another area of the Ferrara Province (COD) reclaimed almost a hundred years before those of the VM, we noted that the soils pass from sub-acid to sub-alkaline conditions with lower salinity and OM content.
2. Batch solubility tests showed a decrease of Ni solubility from recently (VM) to evolved reclaimed soil (COD). COD soils have values of $\log K_d$ higher than VM soil and the latter are correlated with the OM content. Ni concentration in the VM soils is geogenic and at the moment probably bounded to the OM due to OM's retention capacity.
3. The study confirms the results of Mastrocicco et al. (2016) that report the temporal and spatial variations of heavy metals in a shallow aquifer belonging to a marsh saline environment reclaimed in modern age and intensively cultivated. Mastrocicco et al. (2016) showed that due to the organic matter content (as reported in our study) and to the water table oscillation, some inorganic micro constituents (such as metals) are present in high concentrations in groundwater of reclaimed lands such as VM.

Acknowledgements

Authors thank Francesco Droghetti for their support. This work has been supported by EC LIFE+ funding to ZeoLIFE project (LIFE+10 ENV/IT/000321) and by the project ALPIMED (PIE-CSIC-201530E082).

References

Albanese, S., Sadeghi ,M., Lima, A., Dinelli, E. Valera, P., Falconi, M., et al. (2015). GEMAS: Cobalt, Cr, Cu and Ni distribution in agricultural and grazing land soil of Europe. *Journal of Geochemical Exploration*, 154, 81-93.

Amorosi, A. (2012). Chromium and nickel as indicators of source-to-sink sediment transfer in a Holocene alluvial and coastal system (Po Plain, Italy). *Sedimentary Geology*, 280, 260-269.

Amorosi, A., Centineo ,M.C., Dinelli, E., Lucchini, F., Tateo, F. (2002). Geochemical and mineralogical variations as indicators of provenance changes in Late Quaternary deposits of SE Po Plain. *Sedimentary Geology*, 151, 273-292.

Amorosi, A., Guermandi, M., Marchi, N., Sammartino, I. (2014). Fingerprinting sedimentary and soil units by their natural metal contents: A new approach to assess metal contamination. *Science of the Total Environment*, 500-501, 361-372.

Amorosi, A., Sammartino, I. (2007). Influence of sediment provenance on background values of potentially toxic metals from near-surface sediments of Po coastal plain (Italy). *International Journal of Earth Sciences*, 96, 389-396.

Bianchini, G., Laviano, R., Lovo, S., Vaccaro, C. (2002). Chemical-mineralogical characterisation of clay sediments around Ferrara (Italy): A tool for an environmental analysis. *Applied Clay Science*, 21, 165-176.

Bianchini, G., Natali, C., Di Giuseppe, D., Beccaluva, L. (2012), Heavy metals in soils and sedimentary deposits of the Padanian Plain (Ferrara, Northern Italy): Characterisation and biomonitoring. *Journal of Soils and Sediments*, 12, 1145-1153.

Bianchini, G., Di Giuseppe, D., Vittori Antisari, L. (2013a). Soil-water interaction in soils of the Po River Plain (Ferrara, Northern Italy): Insights on heavy-metal mobility and phytoavailability. *Periodico di Mineralogia*, 82, 163-176.

Bianchini, G., Di Giuseppe, D., Natali, C., Beccaluva, L. (2013b). Ophiolite inheritance in the Po Plain sediments: Insights on heavy metals distribution and risk assessment. *Ofioliti*, 38, 1-14.

Bini, C. & Zilocchi, L. (2004). Soil evolution in recently reclaimed wetland areas of Northeast Italy. *Agrochimic*a, 48, 213-221.

Colombani, N., Mastrocicco, M., Di Giuseppe, D., Faccini, B., Coltorti, M. (2015). Batch and column experiments on nutrient leaching in soils amended with Italian natural zeolitites. *Catena*, 127, 64-71.

Connor, R.F., Chmura, G.L., Beecher, C.B. (2001). Carbon accumulation in Bay of Fundy salt marshes: Implications for restoration of reclaimed marshes. *Global Biogeochemical Cycles*, 15, 943-954.

Danielson, R.E. & Sutherland, P.L. (1986). Porosity. In A. Klute (Ed.), *Methods of Soil Analysis: Part 1-Physical and Mineralogical Methods* (pp. 443-461). Madison, WI: SSSA Book Series. Soil Science Society of America, American Society of Agronomy.

Di Giuseppe, D., Bianchini, G., Faccini, B., Coltorti, M. (2014a). Combination of wavelength dispersive X-ray fluorescence analysis and multivariate statistic for alluvial soils classification: A case study from the Padanian Plain (Northern Italy). *X-Ray Spectrometry*, 43, 165-174.

Di Giuseppe, D,. Bianchini, G., Vittori Antisari, L, Martucci, A, Natali, C, Beccaluva, L. (2014b). Geochemical characterization and biomonitoring of reclaimed soils in the Po River Delta (Northern Italy): Implications for the agricultural activities. *Environmental Monitoring and Assessment* 186, 2925-2940.

Di Giuseppe, D., Faccini, B., Mastrocicco, M., Colombani, N., Coltorti, M. (2014c). Reclamation influence and background geochemistry of neutral saline soils in the Po River Delta Plain (Northern Italy). *Environmental Earth Sciences*, 72, 2457-2473.

Di Giuseppe, D., Melchiorre, M., Tessari, U., Faccini, B. (2016). Relationship between particle density and soil bulk chemical composition. *Journal of Soils and Sediments*, 16, 909-915.

Dinelli, E., Summa, V., Tateo, F. (2007). Geochemical and mineralogical proxies for grain size in mudstones and siltstones from the Pleistocene and Holocene of the Po River alluvial plain, Italy. *Special Paper of the Geological Society of America*, 420, 25-36.

Doody, J.P. (2001). *Coastal Conservation and Management: an Ecologicl Perspective*. Kluwer, Academic Publisher, Boston.

Fernández, S., Santín, C., Marquínez, J., Álvarez, M.A. (2010). Saltmarsh soil evolution after land reclamation in Atlantic estuaries (Bay of Biscay, North coast of Spain). *Geomorphology*, 114, 497-507.

IUSS (International Union of Soil Sciences) Working Group WRB (2007). *World reference Base for Soil Resources 2006*. Rome: FAO.

Lal, R. (2001). World cropland soils as a source or sink for atmospheric carbon. *Advances in Agronomy*, 71, 145-191.

Li, J., Pu, L., Zhu, M., Zhang, J., Li, P., Dai, X., Xu, Y., Liu, L. (2014). Evolution of soil properties following reclamation in coastal areas: A review. *Geoderma*, 226-227, 130-139.

Luo, X.S., Zhou, D.M., Liu, X.H., Wang, Y.J. (2006), Solid/solution partitioning and speciation of heavy metals in the contaminated agricultural soils around a copper mine in eastern Nanjing city, China. *Journal of Hazardous Materials*, 131, 19-27.

Malferrari, D., Laurora, A., Brigatti, M.F., Coltorti, M., Di Giuseppe, D., Faccini, B., Passaglia, E., Vezzalini, M.G. (2013). Open-field experimentation of an innovative and integrated zeolitite cycle: Project definition and material characterization. *Rendiconti Lincei*, 24, 141-150.

Mastrocicco, M., Colombani, N., Di Giuseppe, D., Faccini, B., Ferretti, G., Coltorti, M. (2016). Abnormal trace element concentrations in a shallow aquifer belonging to saline reclaimed environments, Codigoro (Italy). *Rendiconti Lincei*, 27, 95-104.

Melchiorre, M., Di Giuseppe, D., Tessari, U., Faccini, B. (2016). Particle density distribution in a fluvial floodplain. *Rendiconti Online Societa Geologica Italiana,* 39, 163-165.

Saljnikov, E., Cakmak, D., Rahimgdieva, S. (2013). Soil organic matter stability as affected by land management in Steppe Ecosystem. In M.C. Hernandez Soriano (Ed.) *Soil Processes and Current Trends in Quality Assessment* (pp. 269-310). Croatia: INTECH Journals.

Stefani, M. & Vincenzi, S. (2005). The interplay of eustasy, climate and human activity in the late Quaternary depositional evolution and sedimentary architecture of the Po Delta system. *Marine Geology* 222-223, 19-48.

Syrovetnik, K., Malmström, M.E., Neretnieks, I. (2007). Accumulation of heavy metals in the Oostriku peat bog, Estonia: Determination of binding processes by means of sequential leaching. *Environmental Pollution*, 147, 291-300.

Tiessen, H., Moir, J.O. (1993). Total organic carbon. In M.E. Cater (Ed.), *Soil Sampling and Methods Analysis.* (pp. 187-200). Ann Arbor, MI: Lewis Publisher.

Utset, A., & Borroto, M. (2001). A modeling-GIS approach for assessing irrigation effects on soil salinisation under global warming conditions. *Agricultural Water Management*, 50, 53-63.

Vittori Antisari, L., Carbone, S., Gatti, A., Vianello, G., Nannipieri, P. (2013). Toxicity of metal oxide (CeO_2, Fe_3O_4, SnO_2) engineered nanoparticles on soil microbial biomass and their distribution in soil. *Soil Biology and Biochemistry*, 60, 87-94.

Figure captions

Fig. 1 Sketch map of the eastern Ferrara province and the Po River Delta. Dashed lines delimit the reclaimed salt marshes. VM, Valle del Mezzano; COD, Codigoro.

Fig. 2 Top – simplified geomorphological map of the Po River Delta. Bottom – Temporal evolution of the Po River Delta morphology due to the reclamation activities.

Fig. 3 Total Ni concentration of the VM and COD samples. A and B correspond to topsoil and subsoil levels, respectively.

Fig. 4 OM vs. $logK_d$ of VM samples plot showing the correlation (expressed as R^2) between the soluble Ni content and the organic matter present in the soils.

Table captions

Table 1 Total Ni concentrations in the VM and COD soils. OM, organic matter; EC, electric conductivity. A (0-20 cm below the ground level) and B (20-50 cm below the ground level) horizons are the topsoil and subsoil, respectively.

Table 2 Results of the leaching test for the VM and COD soils.

Supplementary material

Supplementary Figure 1: VM sampling sites studied in Di Giuseppe et al., 2014. Black dots represent the sampling sites of this study.

Supplementary Figure 2: COD sampling site used in this study.

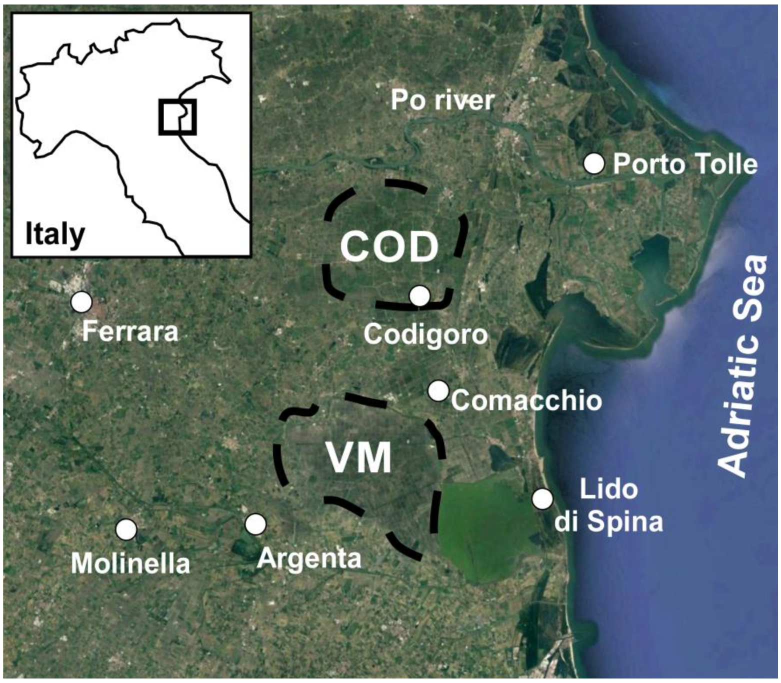


Fig. 1 Sketch map of the eastern Ferrara province and the Po River Delta. Dashed lines delimit the reclaimed salt marshes. VM, Valle del Mezzano; COD, Codigoro.

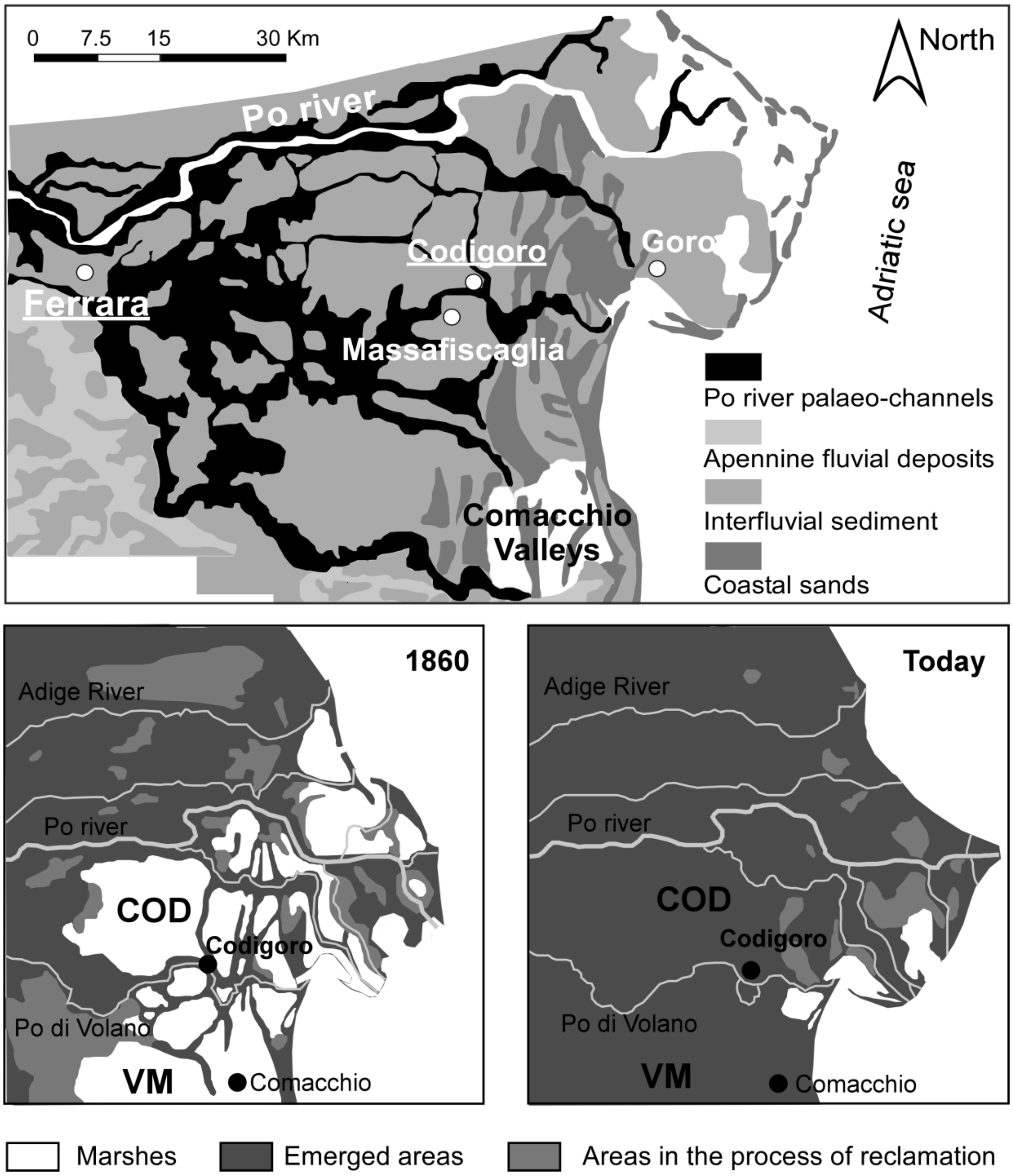


Fig. 2 Top – simplified geomorphological map of the Po River Delta. Bottom – Temporal evolution of the Po River Delta morphology due to the reclamation activities.

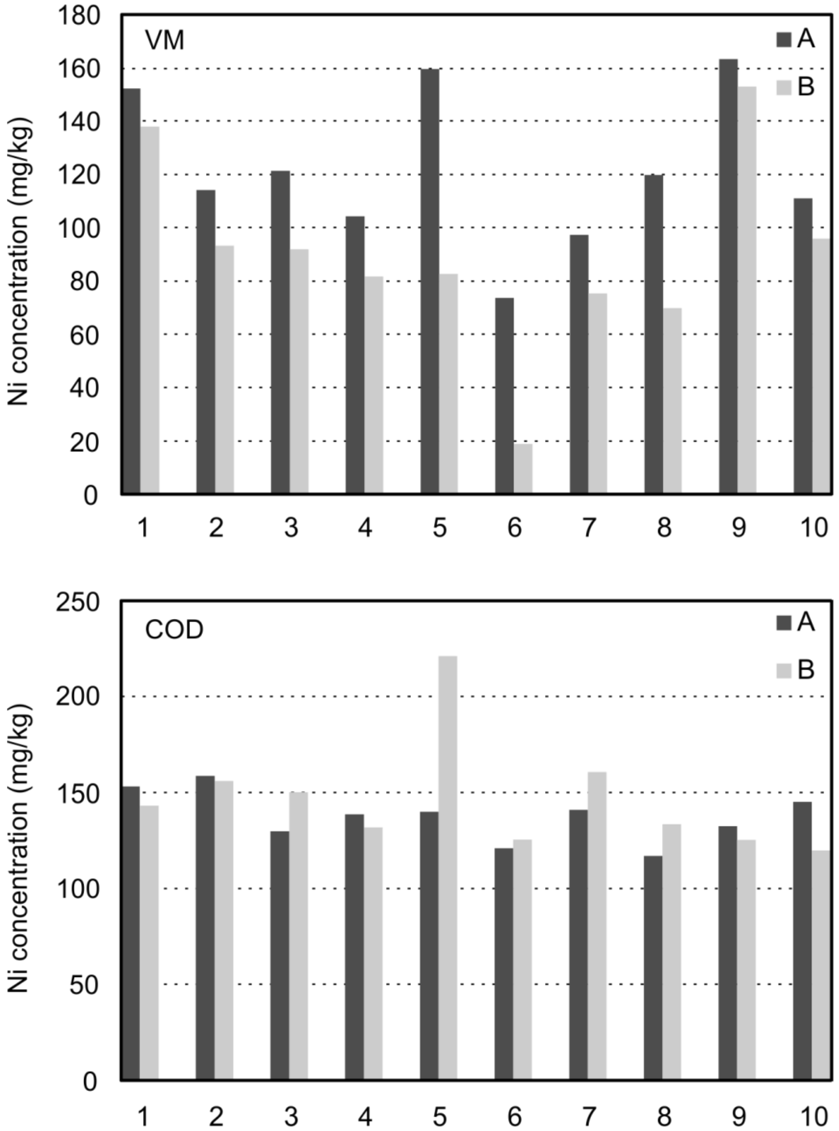


Fig. 3 Total Ni concentration of the VM and COD samples. A and B correspond to topsoil and subsoil levels, respectively.

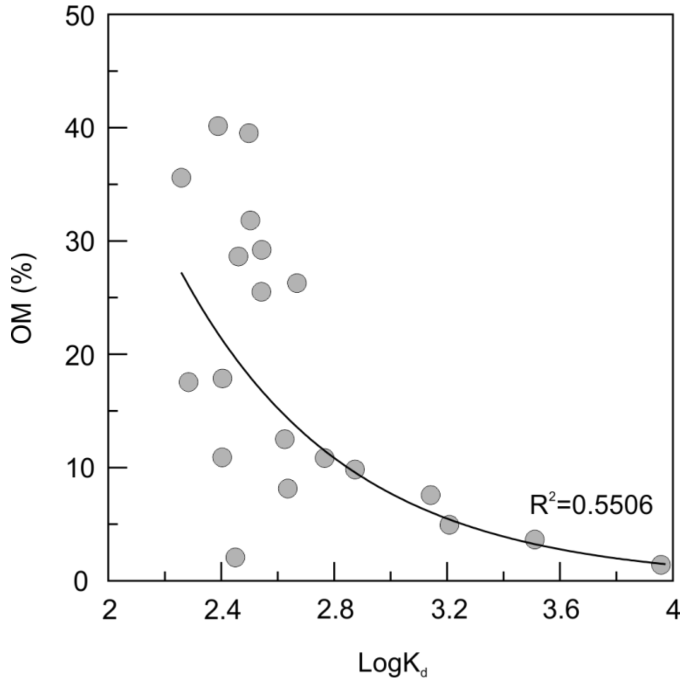


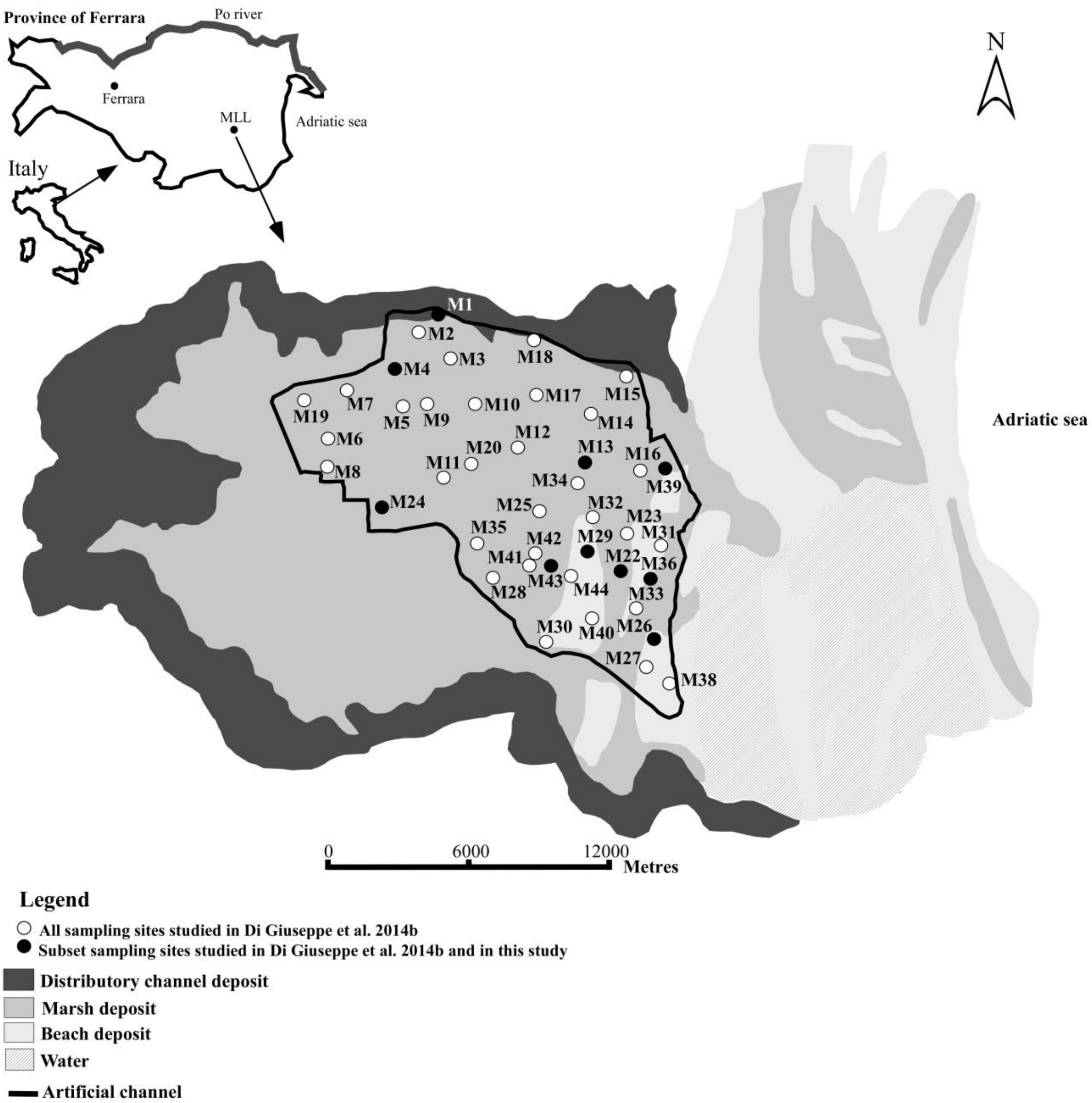
Fig. 4 OM vs. logK_d of VM samples plot showing the correlation (expressed as R^2) between the soluble Ni content and the organic matter present in the soils.

VM								COD							
Number of sample	Label	Horizon	Ni in soil (mg/Kg)	OM (%)	pH	EC (mS/cm)	Clay %	Number of sample	Label	Horizon	Ni in soil (mg/Kg)	OM (%)	pH	EC (mS/cm)	Clay %
1	M1	A	152	9.8	6.5	1.8	58.1	1	C1	A	153	8.2	6.5	1.6	39.0
2		B	138	4.9	5.9	8.0	48.5	2		B	143	7.6	6.0	1.2	40.8
3	M4	A	114	3.6	6.0	1.7	32.7	3	C2	A	159	8.0	7.7	1.4	48.5
4		B	93.3	1.1	5.8	1.2	17.2	4		B	156	7.8	6.8	1.4	48.0
5	M13	A	121	31.8	7.7	5.8	66.4	5	C3	A	130	6.7	6.3	1.7	38.1
6		B	91.9	12.5	6.3	4.4	64.3	6		B	150	6.4	6.5	1.8	58.1
7	M22	A	104	39.5	6.8	5.0	63.2	7	C4	A	139	8.0	6.4	1.7	44.0
8		B	81.7	17.9	5.6	6.3	57.0	8		B	132	7.6	6.5	2.7	36.1
9	M24	A	160	26.3	6.7	5.1	62.9	9	C5	A	140	10.0	6.0	1.4	44.7
10		B	82.7	28.6	5.5	6.6	78.5	10		B	221	9.5	6.8	1.8	50.3
11	M26	A	73.6	10.9	6.4	0.7	74.3	11	C23	A	121	8.2	8.3	1.1	21.7
12		B	18.9	2.1	5.2	1.2	79.0	12		B	125	7.6	8.6	1.5	22.5
13	M29	A	97.3	40.1	7.2	2.1	34.1	13	C24	A	141	9.8	7.6	1.8	19.7
14		B	75.3	17.5	6.5	4.5	3.7	14		B	161	9.5	7.9	1.7	20.5
15	M36	A	120	29.2	6.2	3.0	70.6	15	C26	A	117	10.0	8.4	0.7	21.9
16		B	69.8	35.6	6.5	13.5	43.0	16		B	133	9.8	8.2	1.2	21.4
17	M39	A	163	7.6	7.2	2.6	66.1	17	C27	A	133	7.7	8.3	1.4	21.8
18		B	153	10.8	5.8	6.1	80.3	18		B	125	9.3	8.2	1.8	21.5
19	M43	A	111	25.5	6.6	1.6	58.1	19	C28	A	145	8.8	8.2	1.0	21.4
20		B	95.9	8.1	5.9	4.8	55.5	20		B	120	9.0	8.0	3.4	20.9
Mean			106	18	6	4	56	Mean			142	8	7	2	33

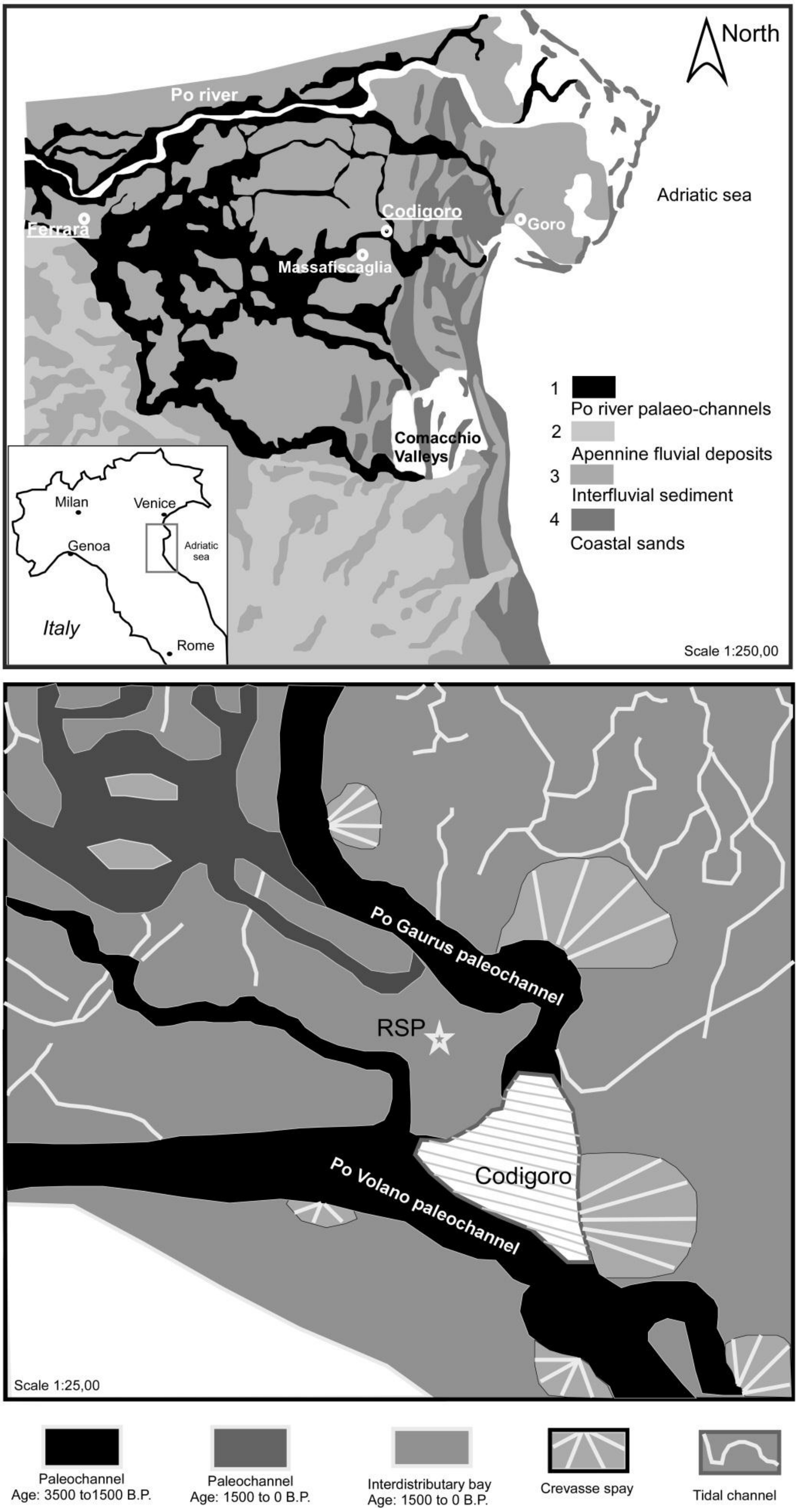
Table 1 Total Ni concentrations in the VM and COD soils. OM, organic matter; EC, electric conductivity. A (0-20 cm below the ground level) and B (20-50 cm below the ground level) horizons are the topsoil and subsoil, respectively.

VM					COD				
Label	Horizon	µg/Kg	Kd	LogKd	Label	Horizon	µg/Kg	Kd	LogKd
M1	A	204	748	2.9	C1	A	232	661	2.8
	B	85	1614	3.2		B	119	1207	3.1
M4	A	35	3241	3.5	C2	A	72	2197	3.3
	B	10	9420	4.0		B	68	2310	3.4
M13	A	381	318	2.5	C3	A	114	1140	3.1
	B	218	422	2.6		B	21	7030	3.8
M22	A	332	315	2.5	C4	A	38	3639	3.6
	B	322	254	2.4		B	16	8481	3.9
M24	A	343	466	2.7	C5	A	29	4753	3.7
	B	286	289	2.5		B	34	6544	3.8
M26	A	291	253	2.4	C23	A	20	6027	3.8
	B	67	282	2.4		B	4	28010	4.4
M29	A	398	245	2.4	C24	A	7	19809	4.3
	B	392	192	2.3		B	5	34854	4.5
M36	A	343	349	2.5	C26	A	17	6960	3.8
	B	385	181	2.3		B	31	4257	3.6
M39	A	118	1386	3.1	C27	A	3	44446	4.6
	B	262	584	2.8		B	2	70117	4.8
M43	A	319	348	2.5	C28	A	22	6658	3.8
	B	222	432	2.6		B	15	7794	3.9
Mean		251	1067	3	Mean		43	13345	4

Table 2 Results of the leaching test for the VM and COD soils.



Supplementary Figure 1: VM sampling sites studied in Di Giuseppe et al., 2014. Black dots represent the sampling sites of this study.



Supplementary Figure 2: COD sampling site used in this study.

409