LIFE PROJECT - SEKRET
LIFE12 ENV/IT/000442

"Sediment ElectroKinetic REmediation Technology for heavy metal pollution removal"

Technical report (Annex to Action C2)

Validation of the demonstrated technology with 6 more types of polluted port sediment - Progress Report 15 May 2015

Annex: Validation of the demonstrated technology with 6 more types of polluted port sediments - Progress Report 15 May 2015

CONTENTS

LIST OF FIGURES

LIST OF TABLES

1.1 Summary

The present report shows and discusses the activities carried out so far in the framework of C2 action, with the aim of evaluating the feasibility of the electro-remediation treatment of sediment samples different from those tested during Action A2.2 and A2.3 .

The investigation was aimed at developing an additional set of laboratory-scale EK cells, designed in order to better elucidate the mechanisms and processes occurring when the electrical field is applied. Stemming from results attained so far, the present experimental campaign was performed by adding chemical agents in one or both the electrodic chambers, and treatment duration was prolonged so as to allow metal migration.

Despite the high treatment duration, all the EK tests were carried out at a high current value, equal to 20 A/m^2, so as to promote the attainment of chemical equilibria favoring metal mobilization.

On the basis of the results attained during Action A2, severe operating conditions, i.e. high current intensity, high chemical dosages, high treatment duration, were adopted in order to improve remediation yields.

The following types of chemical agents will be tested during Action A2: 1) acid solutions; 2) chelating agents; 3) reducing agents. Each sediment sample will be treated by one or more agents, even in combination, on the basis of the outcomes from the characterization stage.

So far, the following activities have been carried out in the framework of Action C2, some of which are currently under way:

- contacts with several Port Authorities and stakeholders (on-going);

- collection of sediment samples from dredging works in different Italian sites (on-going);

- characterization of samples to be tested (on-going);

-design of the new EK cells, equipped with a number of auxiliary systems to improve the EK process monitoring (completed);

- design and implementation of a new system for resistivity data acquisition during the EK test (completed);

- preliminary testing of sediment samples (on-going).

The activities carried out under Action C2 were carried out with the external support of the University of Cagliari, Department of Civil and Environmental Engineering and Architecture.

1.2 Selection of 6 more types of polluted port sediments

So far, four more types of sediment samples have been identified and partly collected for the activities of task C2.

It should be underlined that the identification of additional samples to be analyzed is quite complicated by a number of administrative and technical issues, including the slow and complex procedures to get the permit to have access to the area and to the material, the type of material contamination , the grain size distribution and the feasibility of collecting relatively small amounts to be delivered to the laboratories. In order to identify the three out of six samples, a number of port Authorities and operators were contacted by phone and e-mail, including the Authorities of the following harbors: Civitavecchia, Ravenna, Messina, Napoli, La Spezia, Taranto, Piombino.

The four samples identified and partly collected so far include:

-a sub-sample of Livorno harbor;

-two samples from La Spezia;

-one sample from Napoli (to be collected on July, 15th 2015).

Figure 1 Maps of the harbors

The sites for sediment samples collection were identified on the basis of the support given by Port Authorities and/or operators working for sediment dredging in the abovementioned sites, as well as considering the information on the nature and concentration of contaminants and particle size distribution. In particular, the results of the characterization campaign carried out in the past on sediment samples from La Spezia and Napoli showed that the material is fine-graded and the metal concentration is not negligible. Thus, given the interest and willingness of the Port Authorities and operators, samples were collected and will be tested in the future.

In particular, University of Pisa has collected during the month of March 2015, two samples from the La Spezia harbor with the help of the local operator involved in dredging activities. Samples have been homogenized and separated into sub-samples that will be sent to Uniroma1 and to University of Cagliari before the end of July. Details on methods and procedures adopted during sample processing

(homogenization and sub-sample preparation) have been already provided in Annex to action A2 of the inception report.

The following sub-samples have been thus prepared by University of Pisa and will be sent to the Universities of Rome and Cagliari:

- 2 sub-samples from La Spezia harbor (approximately 10 kg each). Sediment appear to be composed of fine-graded particles.

- 2 sub-samples from La Spezia harbor (approximately 15 kg each). Sediment appear to be composed of a relevant fraction of fine sand.

- 2 sub-samples from Livorno harbour (approximately 10 kg each). Sediment are composed of fine graded particles.

On July 15th, University of Rome will collect, with the support of the Napoli Port Authorities, an additional sample of sediment. It will be transferred to the University of Rome, where it will be homogenized and divided into two sub-samples according to the abovementioned methods and procedures; one of the two sub-samples will be sent to University of Cagliari.

In the next months, three additional samples will be acquired from the same or different sites, depending on the sediment properties as resulting from already performed characterization campaign, and given the cooperation of the local Authorities.

1.3 Design of the new EK cells

A new series of EK cells was designed in order to evaluate the feasibility of the remediation technology to more sediments samples. The new cells, larger than the ones adopted during action A2, have been designed so as to allow for a thorough investigation of the process, as a number of additional systems for EK system monitoring and characterization have been developed.

The cells are made of plexiglass so as to allow for the visual inspection of the sediment sample during the remediation process.

The detail of the cell size is reported in Figure 2 and Figure 3. Each cell was built as a box with external dimensions of 52Lx9Wx11H (in cm). The thickness of Plexiglas layers was set equal to 1 cm, so as to guarantee an adequate mechanical strength of the cell. Each cell was divided into three compartments, namely the two external electrolyte chambers (anodic and cathodic) where the graphite electrodes aree placed and the central chamber containing the sediment sample to be treated. Each external chamber has inner dimensions approximately 10Lx7Wx10H (in cm) and the central chamber has inner dimensions equal to 30Lx7Wx10H (in cm). It should be noted that the actual filling height of sediment and solution in the three chambers during the runs, is lower and approximately equal to 6 cm, so as to prevent any loss of material during the experiment. Two mobile separation membranes are used in order to separate

the electrodic chambers from the sediment. According to the configuration already adopted during Action A2, the separation membranes include a layer of paper filter, aimed at hindering the migration of sediment particles towards the chambers, coupled with a semi-rigid plastic net aimed at providing the mechanical strength to the unit. In order to minimize the on-set of preferential paths of electrolyte migration, and to reduce the undesired migration of sediment particles towards the electrodes. a Plexiglass framework was designed and build so as to fix the two layers and to place them into the slots. Two graphite electrodes are placed in each chamber and connected to the DC generator, able to displace a constant current in the range 0 - 20 A. The DC generator is also equipped with voltmeter, working in the range 0-60 V

The newly developed monitoring system of the EK process, is composed of two different equipment.

The first one is aimed at allowing the sampling of the liquid solution along the sediment length. Chemical characterization of the circulating electrolytic solution in terms of both pH and elemental composition, will provide useful information on the extent of metal mobilization and migration along the specimen length during the EK treatment. For this purpose, a number of mobile and vertical drainage pipes, with a diameter of 8 mm, are placed along the central chamber of the cell. The pipe size has been chosen considering two contrasting needs, namely the reduction of any significant interference on the EK process and the possibility to sample the liquid solution by means of standard laboratory pipettes.

The second of the two monitoring systems is aimed at improving the measurement of sediment resistivity evolution during the EK test. The analysis of the results gained during Action A2 (see the abovementioned Annex to the inception report), has evidenced the instability of the measurement of resistivity during the large part of the EK tests. In fact, some variations of the resistivity values as measured by the system appeared to be unexpected and hard to be interpreted and justified. Moreover, a number of critical issues have been experienced with the accuracy and robustness of the measurement device and the related data logger. In particular, measurement electrodes polarization and corrosion adversely affected the quality of the data set. The new system applied to the new cell is composed of 5 measurement electrodes (see Figure 4) connected so as to prevent corrosion, and an ad hoc hardware and software for resistivity data acquisition and storage is currently under development using LabView®. The hardware is composed by a chassis where will be inserted the board for data recording, a PC directly connected with the board and the electrodes connected with the chassis. In this mode of operation it is possible control the data in real time. The size of the measurement electrodes was as small as possible (1Wx5Hx0.2L in cm) so as to reduce any interference with the hydraulic and electrical flow along the cell.

At the moment of writing the present report, a round robin phase has been carried out with staff from the geophysical laboratory by using more accurate and precise instruments to measure sample resistivity. Such a phase is aimed at monitoring the effect of both the electrodes polarization and the presence of chemical agents on the quality of the measured data. For this purpose, a dedicated test has been started in order to measure the evolution of the sample resistivity over time by the ad hoc developed system, using a small size cell. The measured values are then compared with the instantaneous measure carried out by means of special electrodes, resistant to polarization, which are removed from the sediment sample as soon as the measurement has been completed. During measurement, moreover, the electric field is removed, so as to avoid any disturbance or interference. The results among the two measurements methods, acquired over a timeframe of more than three months) will be then analysed (presumably during next September and October) and used to improve the method currently adopted for resistivity measurement. At the end of such a phase, a robust method for resistivity measurement and a procedure to interpret the data of resistivity measured with the continuous method based on fixed electrodes, will be reasonably made available.
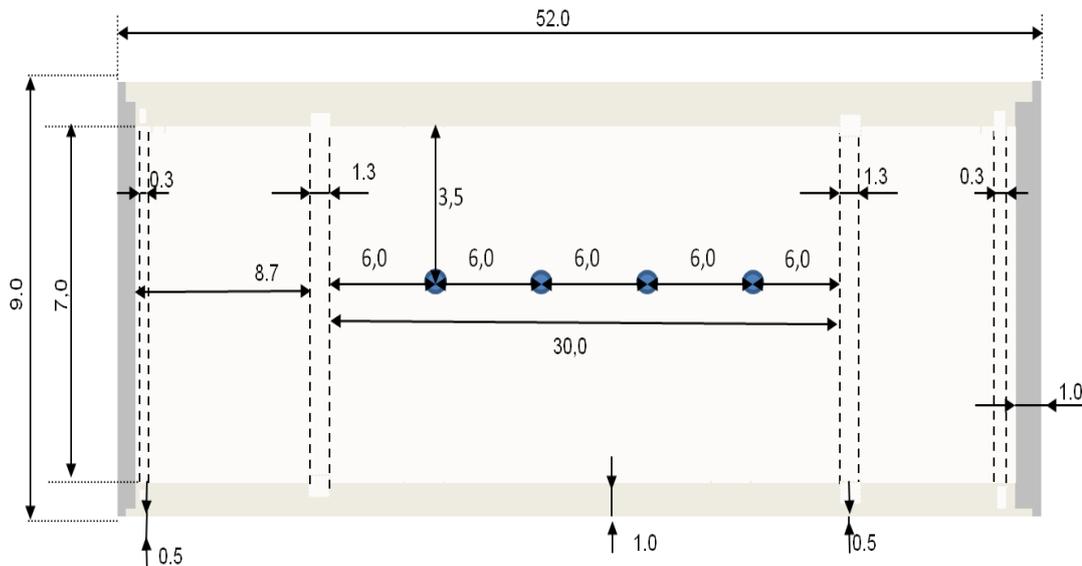

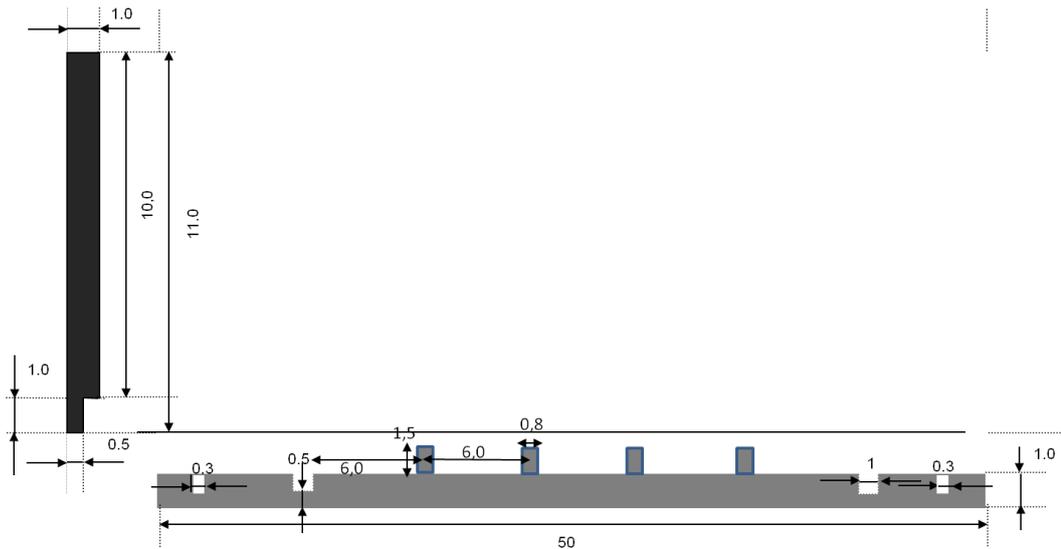**Figure 2** Scheme of the new cell-overview from above (in blue the position of the drainage pipes)

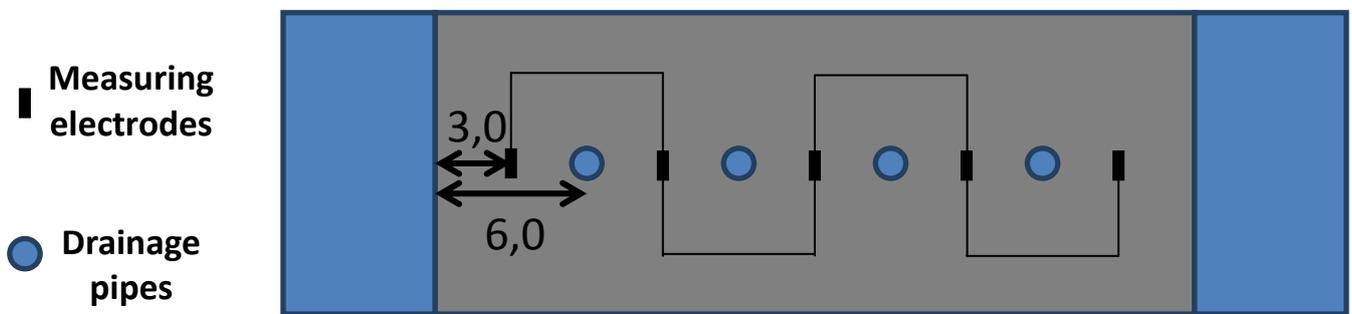**Figure 3** Scheme of the new cell- lateral overview

Figure 4 Scheme of measuring electrodes position (view from above)

1.4 Preliminary EK tests

So far, the EK tests of action C2 were performed on the sub-sample of Livorno harbor using the same experimental cells (see Figure 5) of action A2. All the analytical and test methods adopted have been already described in relation to action A2 (see Annex to action A2 of the inception report), and are thus briefly mentioned in the following tests. Such tests are considered as preliminary and will be compared in the next months with the tests carried out on the above-described large cells. In fact, as for the Action A2, the tests on the small-sized cells are performed to acquire the basic information on the processes governing metal mobilization. The experiments were carried out at a constant DC density of 20 A/m^2, under the testing conditions reported in Table 1. At the end of each test, the electrode solutions were extracted and acidified with 1:1 HNO$_3$ for subsequent chemical analysis; in addition, the sediment sample was extracted and divided into three portions (close to the anodic compartment [S+], central section [Sc] and close to the cathodic compartment [S-]. Each slice was characterized for pH, then weighed, dried until constant weight and ball-milled in view of subsequent chemical characterization.
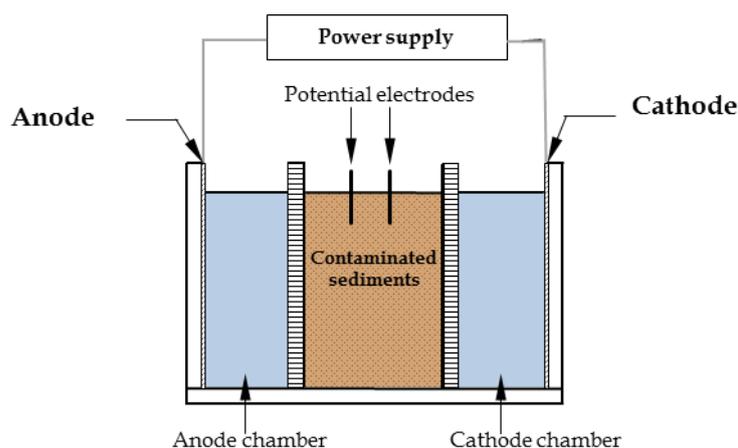
Figure 5 Old series of EK cells

In these tests were tested three different agents in the cathodic chamber: HCl, CH_3COOH, EDTA and for Test 17 NaOH in the anodic chamber.

As we mentioned in action A2, acid solutions were added in order to reduce sediment pH and to promote metal solubilization and migration towards the electrodes. The adding to the cathode has the aim of neutralizing the OH^- generated by electrodic reactions, thus preventing OH^- migration towards the cathode and the decrease of sediment pH. The results of the tests with acid solutions for 7 and 21 days (Action A2) show a negligible sediment acidification and for this reason we have decided to improve the tests duration until 60 and 90 days.

EDTA was tested in order to evaluate the effect on metals mobility and migration. EDTA is known to promote metals solubility through complexation reactions, so that the addition to the system may in principle favor metals removal from the matrix. The dosage was calculated assuming that all the Ca, Mg, Fe as well as the contaminants of interest, were available for complex formation through a 1:1 molar ratio reaction. The amount of EDTA required to react with all the considered elements, was then increased of a safety factor equal to 2. Moreover in test 17 we used NaOH in anodic chamber for the neutralization of H^+ generated at the anode and so prevent the precipitation of EDTA (soluble in pH range 4-14) close to the anode.

Table 1. EK tests

TEST	ANOLYTE	CATHOLYTE (test duration in brackets)	AMOUNT OF CONDITIONING AGENT (*)
15	H_2O	HCl (60 d)	H
16	H_2O	EDTA (60 d) ◆	^
17	H_2O+NaOH▪	EDTA (60 d) ◆	^
18	H_2O	CH_3COOH (90 d)	H

(*) H: amount required to neutralize OH- generated at the cathode and to attain pH=3 during ANC;
(^) amount added so as to complex Ca, Mg and metals, assuming a molar ratio of 1:1.
(◆)CH_3COOH used at the cathode for 7 d to neutralize the OH^- ions generated and mobilize major elements, then replaced by EDTA for the rest of the test; NaOH added to the anolyte from day 28 to neutralize the H^+ generated thus preventing EDTA precipitation
(▪)amount required to neutralize H^+ generated at the anode

The preliminary lab-scale EK tests of action C2 were performed by means of a system composed of the following units:

-Plexiglas EK cell;

-DC generator;

-graphite electrodes;

--auxiliary equipment (including, for example, wires and cables, glass and PET beakers, pipettes, crucibles, compaction loads, glass and paper filters, chemicals agents, pH-meters, muffle, oven, analytical and technical balances).

A picture of the EK cell filled with a new sediment sample in the central chamber is reported in Figure 6

Figure 6. Details of the Plexiglas EK cell filled with new sediment in the central compartment (lateral view)

1.5 Preliminary EK tests results

In the present paragraph, results of EK tests in terms of contaminants mobilization are shown and discussed.

As depicted in see Figure 7, Test 15 evidenced good results in terms of removal efficiency for Cd , Cu, Ni and Zn.. Under the tested conditions, Cd was observed to be accumulated near the cathodic chamber. Using HCl at high dosages did not result into a significant mobilization ofCr, probably due to its oxyanionic behaviuor.The appreciable acidification of the solid matrix (see the pH curves in Figure 7) occurred when HCl is added at the highest dosage, probably favoured Cr precipitation or adsorption on sediment particles.

For the other metals of concern, it is interesting to note that migration occurred in general towards both the electrode compartments (Figure 8). Such a result suggests that formation of Cl-metal complexes of either charges has occured.
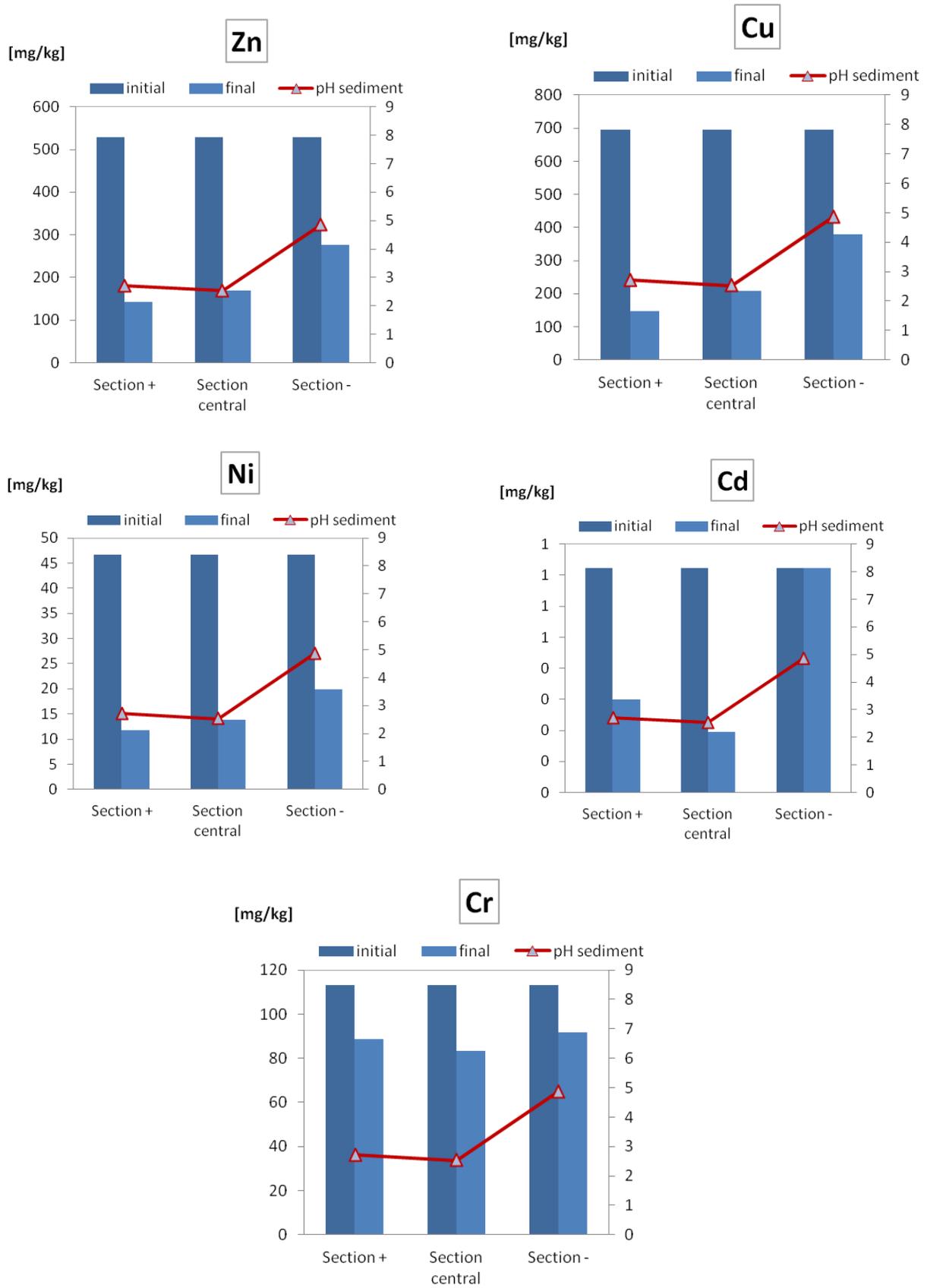
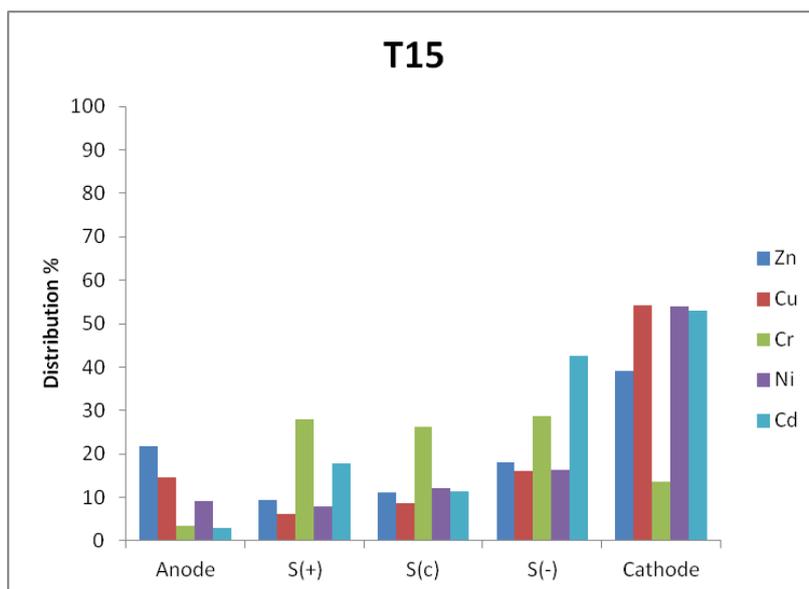**Figure 7**. Residual metal content – test 15

Figure 8 Distribution of the metals in the compartments-T15

Results of test 16 evidenced that, for the investigated sediment sample, the sole addition of EDTA is not able to promote metal mobilization, even at long treatment duration. The final content of metals along the specimen revealed that the migration of EDTA complexes through the sediment slightly promoted the movement of metals towards the anode. It is worth underline that Zn, Cu, Cr and Cd appeared to accumulate in the section (+), so that it could be hypothesized that their migration has likely occurred in the form of negative-EDTA complexes; however, when the complexes reached the section close to the anode, the low pH values caused the precipitation of EDTA (see Figure 9 for pH evolution along the specimen). Thus, both a physical and chemical barrier acetd limiting EDTA migration towards the electrodic chamber. The existence of a physical barrier caused by EDTA precipitation was so relvant that it could have been detected also by visual inspection, as shown in Figure 10.

Among the investigated metals, Ni only was found to be able to reach the anode compartment, even if the extent of migration was slight.
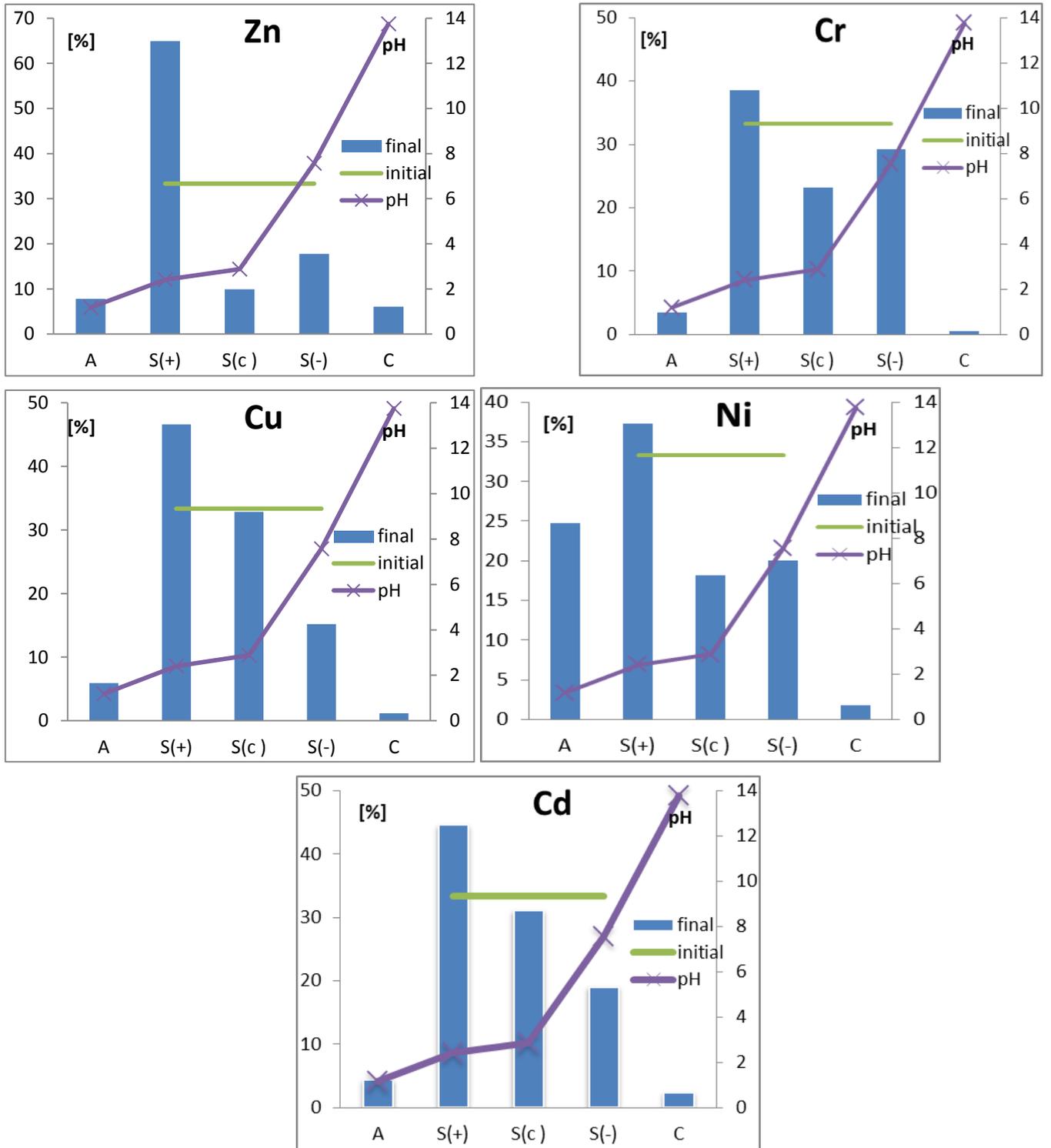
Figure 9. Residual metal content – test 16

Figure 10. precipitation of EDTA close to anodic chamber – test 16

In order to overcome the adverse effect of EDTA precipitation, hindering metals removal from the specimen, an alkaline solution containing NaOH was added to the anodic chamber so as to avoid severe acidification of the solution in the sediment region close to the anolyte and to prevent EDTA precipitation. The results confirmed the appropriateness of the selected operating conditions for the sediment tested in the present set of laboratory runs. A strong removal of contaminants from the whole test cell was in fact observed under the tested conditions, particularly for Ni and Zn. The metals of concern were found to migrate along the specimen and to be able to reach the cathodic compartment within the test duration. Increasing the pH conditions of the circulating solution in the anodic region of the sediment samples was effective in contrasting EDTA precipitation, so that the effect of the chelating agent on the remediation yield was not hindered. Such a result, combined with the results from test 16, confirmed the pivotal role of pH on the processes and mechanisms acting during sediment remediation, even under the effect of an intense electric field.
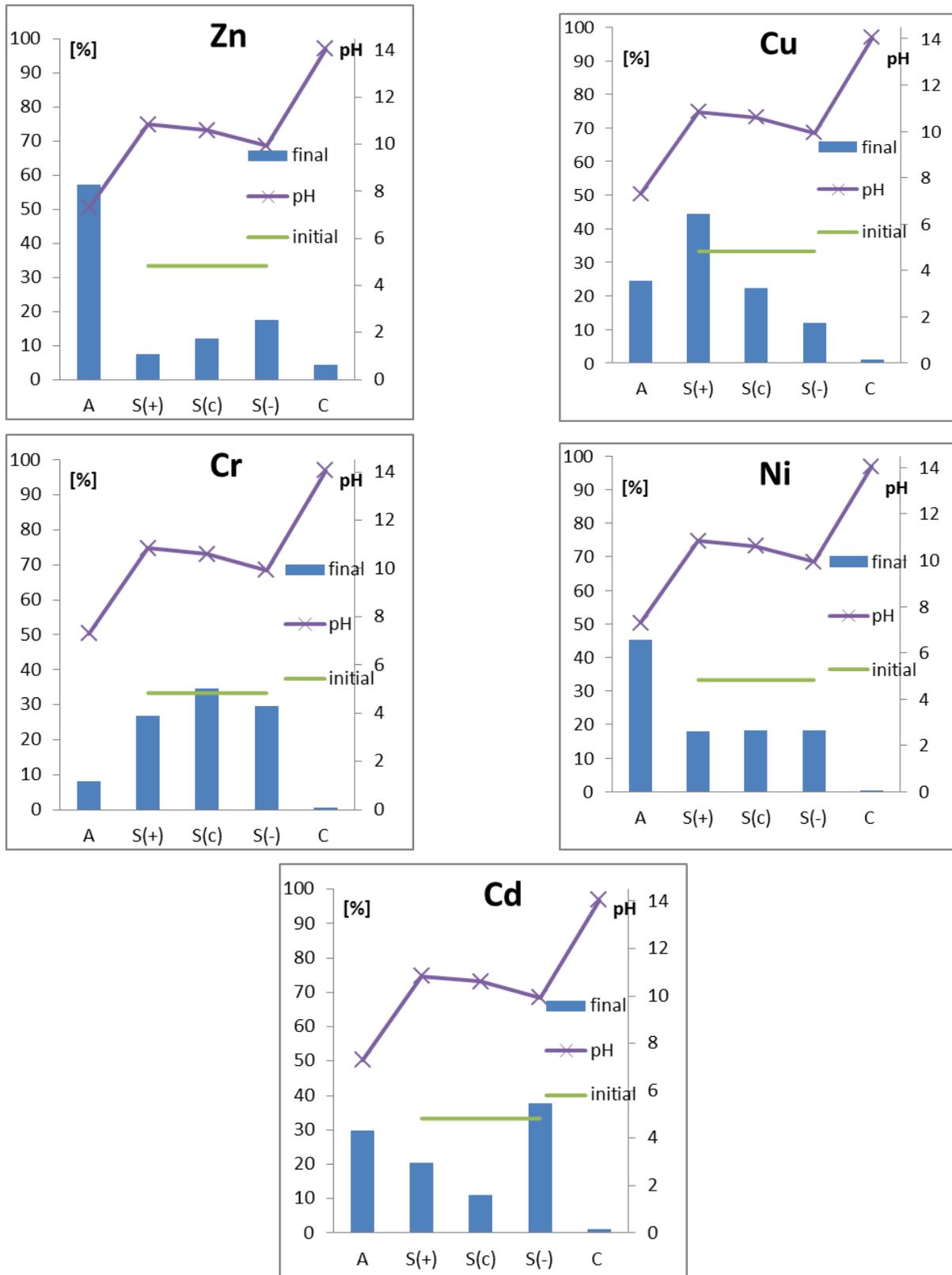
Figure 11. Distribution of metal content – test 17

In Test 18, the effect of treatment duration on the remediation yield that could be attained by using a weak acid, namely acetic acid, was tested by prolonging the treatment duration up to 90 days.

The results showed that at high treatment duration and weak acid dosage, the metals of concern are positive charged and migrate towards the cathode (see Figure 12). The treatment duration was sufficient to let the metals reach the cathodic chamber, even if a slight accumulation of Cu close to the cathodic chamber was observed. However, similarly to HCl, acetic acid was not able to promote Cr mobilization, as very low pH values were attained along the specimen, ranging from 3 to 3.3, in correspondence of which Cr is likely to be present as a precipitate (Figure 13) .
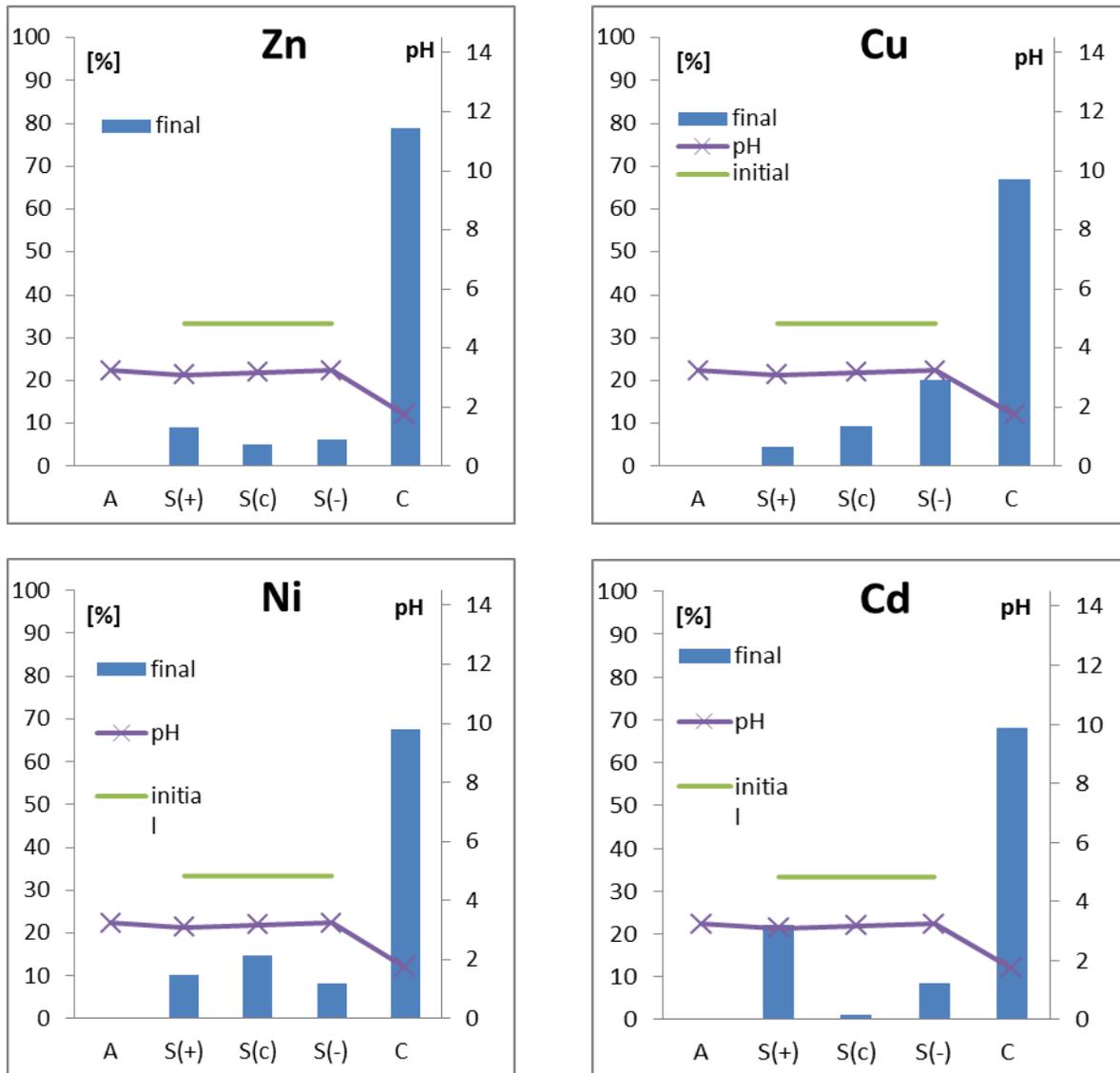

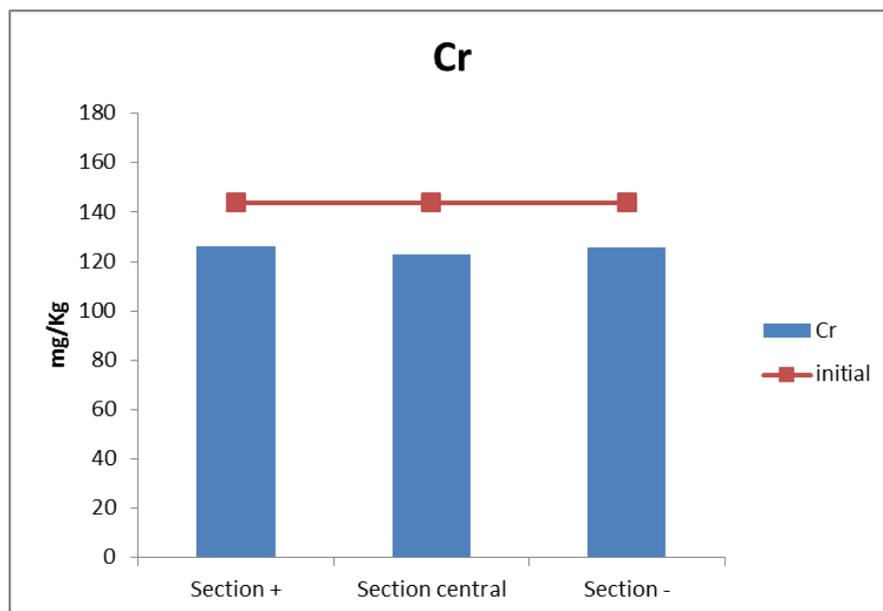**Figure 12.** Distribution of metal content – test 18

Figure 13. Amount of Cr in the sediment sections – test 18

1.6 On-going activities

At the time of writing, the following activities are in progress or will be started in the next weeks:

- to collect the sediment sample from the Napoli harbor (on July 15th 2015);

- to homogenize the sediment sample from the Napoli harbor and send one of the sub-sample to the University of Cagliari;

- - to complete the manufacturing and put into operation of the large cells, both at University of Rome and University of Cagliari;

- to complete the check of the system for resistivity monitoring using more precise and accurate instruments;

- to deliver the La Spezia sediment samples from University of Pisa to University of Rome and University of Cagliari;

- to start chemical and physical characterization of sediment samples from Napoli and La Spezia according to the test methods and procedures described in the abovementioned inception report;

The ending date of the above described activities is planned for the end of December 2015.

Since the end of September, the following actions will be started:

- EK tests in the large cells on the sediments from Napoli and La Spezia;

- start and/or complete the chemical characterization of the sediment after the EK treatment;

- start the procedure to collect three more sediment sample during the early months of 2016.