Leaching tests: useful tools for the risk assessment of contaminated sediments

Damiano Centoli(1), Rob NJ Comans(2), Stefania Gaudino(1), Chiara Galas(1) and Maria Belli(1)

(1) Agenzia per la Protezione dell’Ambiente e per i Servizi Tecnici (APAT), Rome, Italy
(2) Energy Research Centre of The Netherlands, Petten, The Netherlands

Summary. In recent years, the importance of trace metal mobile fractions rather than total contents in environmental matrices is increasing in risk assessment evaluation of contaminated sites. In this study different leaching/extraction tests, aimed at the measurements of mobile fractions of trace metals and standardized at European Committee for Standardization (CEN) for the characterization of waste, have been compared with those adopted by the Italian legislation for soils. All these procedures have been applied on Venice Lagoon sediments, in order to extend the appliance of these methods to sediments and to verify the consistency of the results when different leaching tests are applied on the same sample. The results show that these tests can be applied successfully to sediments and confirm that leaching/extraction methods based on the main parameters controlling the remobilisation of trace metals are useful tools for risk-assessment, because they can allow a “transparent” interpretation in the light of key environmental variables (such as pH and DOC) controlling metal mobility. Further the use of geochemical models in support to leaching allows the assessment of trace metals mobility in the long-term.

Key words: leaching, trace metal, speciation, sediments, Venice Lagoon, risk-assessment.

INTRODUCTION

Sediments constitute the principal sink for trace metals in aquatic systems. The chemical physical characteristics of the environment regulate the metal chemical forms bound to the sediments and their potential for remobilisation. Any variation of environmental conditions can lead to the release of the mobile fractions into the sediment water phase. From the sediment water phase, the metals can become available to organisms living in the water system.

In recent years, the importance of trace metal mobile fractions rather than total contents in environmental matrices is increasing in risk assessment evaluation of contaminated sites. In this framework, metal speciation studies and different leaching and extraction methods have been developed.

Sequential chemical extraction methods are generally applied to sediments [1-4]. In this context, fractions of trace metals in different chemical forms are operationally defined through the determination of extractable element fractions, using several reagents (salt solutions, weak and strong acids, reducing and oxidising agents) in sequence. In these methods, the extractable trace metal fractions are strictly dependent on the extraction procedure applied. In the environment metal speciation and mobility in sediments.
soils and waste are controlled by fundamental environmental variables particularly pH, redox potential, dissolved organic carbon (DOC), salinity, and specific metal binding sites [5]. Leaching/extraction methods based on the main parameters controlling the remobilisation of trace metals in the environment can allow a “transparent” interpretation in the light of key environmental parameters controlling metal mobility. The use of geochemical models in support to leaching and speciation measurements allows the assessment of trace metals mobility in the long-term. Furthermore, modelling contributes to the interpretation and selection of the most appropriate methods for mobility measurements in different environments.

The Italian Environmental Protection Agency (Agenzia per la Protezione dell’Ambiente e per i Servizi Tecnici, APAT), in collaboration with the Energy Research Centre of the Netherlands (ECN), has developed a project (SOILLEACH) focused on the selection and application of relevant leaching/extraction methods of trace metals from sediments, soils and waste. In the project different leaching tests standardized at the European Committee for Standardization (CEN) for the characterization of waste have been compared with the leaching and extraction procedures adopted by the Italian legislation for soils and wastes [6-8]. All these procedures have been applied on soils and sediments, in order to extend the application of these test methods to sediments (horizontal approach) and to verify the consistency of the results when different leaching tests are applied on the same matrix sample.

In this paper the preliminary results of the comparison between leaching and extraction procedures, adopted by the Italian legislation [6, 7], the pH-stat test [9] and the 2 step CEN method [10] applied to Venice Lagoon sediment are reported. Furthermore a short description of the application of geochemical modelling is given.

MATERIALS AND METHODS

Sediment sampling and sample treatment

Venice Lagoon sediment samples were collected with a corer in an area near the railway and road bridge in front of Porto Marghera industrial site. The samples constituted by the superficial layer of sediments were frozen and transported with dry ice until the starting of analysis in order to maintain the natural environmental conditions. The natural pH of the sample was 8.6 while the dry matter content was 57%. The leaching tests were applied on the sediment laboratory samples without any further treatment in order to eliminate any possibility of redistribution of metals between different phases due to air oxidation.

Leaching tests

The two plant-availability leaching tests, suggested by the Italian legislation for soil analysis [6, 7], were originally developed for different soil types. The first method [6], originally developed for calcareous soil, is a batch extraction of metals (Cd, Cu, Ni, Pb, Zn) by a DTPA (diethylenetriaminopentaacetic acid)/CaCl₂/triethanolamine solution with a pH of 7.3. The procedure is the same proposed by Lindsay and Norwell [11] and is based on the chelating property of DTPA while the presence of calcium chloride precludes the dissolution of CaCO₃ and the release of occluded metals which are normally not available to plants [12]. This is a batch extraction of the solid sample with a liquid to solid (L/S) ratio of 2 l/kg and an equilibration period of 2 hours; after centrifugation the solution were diluted to 100 ml and analysed by ICP-AES to obtain the concentration of the target metals. The second method [7], originally developed for acid soil, is a batch extraction of Cd, Cu, Ni, Pb, Zn by an EDTA (ethylenediaminetetraacetic acid)/ammonium acetate solution at pH 4.65. The procedure is the same proposed by Lakanen and Ereviö [13] in which the chelating agent EDTA can dissolve the exchangeable element fraction of metals and also the element fraction forming organic matter complexes and the one fixed on the soil hydroxides. This is a batch extraction of the solid sample with a liquid to solid (L/S) ratio of 5 l/kg and an equilibration period of 30 minutes; after centrifugation the solution were diluted to 100 ml and analysed by ICP-AES to obtain the concentration of the target metals.

Both these availability tests have been compared to the fundamental leaching properties as revealed by the pH-stat test described in detail in the standard prEN14997 for the characterization of waste by CEN [9]. With this test, 8 test portions of the same test sample were subjected for 48 hours to batch leaching in acid-cleaned 300 mL PTFE vessels at various pH values between 2 and 12, using a liquid to solid (L/S) ratio of 10 l/kg and a computerized pH-stat system in order to maintain constant the pH value. Suspensions were kept in contact with an N₂ atmosphere in order to maintain the anoxic conditions of the sediment. Solutions of 1 M HNO₃ and NaOH (analytical grade) were used to adjust the pH of the suspensions. After the equilibration period, the suspensions were filtered through 0.2 µm membrane filters. The filters were precleaned with Nanopure water. The clear filtrates were acidified with concentrated HNO₃ (suprapure) and analyzed by ICP-AES to obtain solution concentrations of many elements. In addition, the 2-step CEN compliance test EN12457-3 [10] for granular waste materials has been applied on the sediment sample. This CEN test can quantify contaminant emission (i.e. the leached amount) from (contaminated) soil and sediment as a function of the extent of contact with water that is the L/S ratio and/or time (Figure 1). This leaching tests can be useful to predict the release pattern in long term. The standard CEN EN12457-3 describes the 2-step batch compliance test that provides informa-
tion on the leaching with deionised water of granular wastes and sludges under the specified experimental conditions, particularly a liquid/solid (L/S) ratio of 2 l/kg dry matter and subsequently of 8 l/kg dry matter. The total time of contact between the sample and the leachant was of 24 hours. After each step the leaching solutions were filtered on 0.45 µm membrane filters. The analysis of the two eluates produced by the leaching test provided the concentrations of the constituents in each of the two eluates, expressed in mg/l. The final results were expressed as the amount of constituent leached relative to the total mass of the sample, in mg/kg of dry matter.

RESULTS AND DISCUSSION

Figure 2 reports the mass fractions of Cd, Cu, Ni, Pb and Zn leached from the sediment at different pH with the pH-stat test and the comparison of the different leaching and extraction methods applied on the Lagoon sediments.

The V-shaped pH-stat curves in Figure 2 obtained for Ni, Pb and Zn contents are typical for metals and consistent with known solubility-controlling processes such as sorption to organic matter and metal(hydr)oxides in soil or sediment matrix [5]. At low pH the maximum mass fraction of metal that can be leached is reached. This maximum value is often reported as the availability for leaching. At pH values ranging between 7-9 the leached amount is minimum.
An increase in the leached amounts is observed at alkaline pH value. This behaviour is due to the sorption of metals on dissolved organic matter. For lead this increase is less marked. These results are reliable with those of other studies of Venice sediment speciation [14] that with sequential chemical extraction found for Ni, and Zn a prevailing proportion of the total bound to Fe/Mn oxides/hydroxides and a fraction of around 7-9% bound to organic matter while for Pb this fraction was very low.

The pH-stat curves show that the maximum mass fractions of metals leached from sediment sample is always lower than the total content. This result shows the importance of leaching test in risk assessment studies. For all elements, except for Zn, up to 1-2 orders of magnitude differences are observed between the maximum concentration leached and the total amount. These results imply that only <1-10% of the total amount of these contaminants are available for leaching. On this basis, the determination of total metals contents in sediments could greatly overestimate the metal fractions which are effectively available for release from the solid matrix. Cd shows a pH-stat curve with the leached amount almost independent from pH in the range from 6 to 12, while at low pH value there is an increase of the leached amount. On the opposite Cu shows a little increase at very alkaline pH while for a broad range of pH value the leached amount is almost constant. The available fraction of Cu is almost entirely associated to dissolved organic matter. The dissolved organic matter (DOC) plays a fundamental role in the release of metals in soil and sediments. In the lagoon sediment the increase of Cu leaching observed at Figure 2 related to pH higher than 10 could be due to the high increase of DOC released in solution (Figure 3). In fact it is known that Cu has great affinity for organic matter because of the capacity to form stable complexes with humic material [15].

The comparison (Figure 2) between different leaching test results (i.e. DTPA and EDTA extractions and CEN 2-step test methods) for Ni and Zn can be explained on the basis of leachate/extract pH. For Pb the result of DTPA extraction can be explained on the basis of leachant pH, while the results of EDTA does not fit with pH. In this case the complexation by EDTA molecule could be responsible of the solubilization of Pb giving a greater leached amount quite near to the metal “availability”. The low amount of Cu leached with EDTA and DTPA extractions could be due to the competitive effect of the humic material present in the sediment. Humic and fulvic acids are more rich of functional groups with high affinity to copper respect to EDTA and DTPA and show an high complexing capacity for copper at pH values around 5 and 7 [15] that are quite the same of the leaching test applied.

Figure 3 shows Fe, As, Mo and V concentrations determined in the leaching solutions after 48 hours of equilibrium between sediment and leaching solutions at different pH. The pH-stat curves for As, V and Mo show a maximum or very high leached amount at very alkaline pH; this is a typical leaching behaviour of metals whose oxyanions forms are very important in sediments and soils [5].
A first evaluation of the reproducibility of the test has been carried out by comparing the results obtained by APAT and ECN laboratories applying the same pH-stat procedure to test portions coming from the same soil test sample. The results obtained for Pb and Cd in the two laboratories are reported in Figure 4. The pH curves show similar behaviours, even if some deviations are present. The differences could be due to the slight different pH value applied during the test in the two laboratories.

**Geochemical modelling**

The pH-stat test provides information on the influence of pH on leaching that are useful to identify the behaviours of chemical components at different pH values under specified experimental conditions.

For long term release prediction in a real scenario, the analytical data from the test may be used as input data for geochemical speciation models, such as for example MINTEQA2 or ORCHESTRA [16-18], to identify the long term solubility control by specific mineral phases. These models are based on thermodynamic data for soils components and phases. The distributions of metals between various mineral solid phases can theoretically be determined by these models. Figure 5 reports the behaviour of iron in the Venice Lagoon sediments assessed with modelling using as input the pH-test results and MINTEQA2. The models results can be used to assess the speciation and the partitioning between free ions and complexes, using additional data on reactive organic matter constituents such as humic and fulvic acids, mineral Fe and Al surfaces that may control metals adsorption to the matrix. In ORCHESTRA, the element interaction with aluminium oxide, iron-oxide, clay surfaces, particulate and dissolved organic matter can be quantified using several mechanistic adsorption models [19].

These models give prediction on metals speciation in soil, sludge and compost and could support the interpretation of the results of metals speciation study and predict the long term release pattern. Future development include the application of those geochemical modelling also to sediments.

**CONCLUSION**

The results obtained by the application of pH-stat test to sediments permit to draw some conclusion.

The CEN prEN14997 pH stat test developed for wastes, can be successfully applied to sediments. The application of this method can simulate the chemical behaviour trends and the availability levels of contaminants due to modified pH condition in the environment. Analysing the resulting pH-stat curves starting from natural pH of the sample, it is possible to assess the release of metals owed to little variations of the environmental pH. This test permits also to evaluate the leaching pattern of DOC that is, together with pH, one of the fundamental parameters affecting metal mobility and availability to organisms.

It is confirmed that it could be better to base the risk assessment not only on total content but also on mobile fraction of metals. In fact if on one side taking in account the total amount of these contaminants provide a better safety measure, on the other side this assumption can over estimate of one or two order the effectively fraction of metals available to release and so toxicological relevant.
Further the test results are the basis for risk assessment evaluation that can be supported by geochemical speciation modelling tools to quantify all relevant species and estimate a related long term release prediction. This approach can go further the claimed speciation possibilities with sequential chemical extraction schemes.

Finally as shown in Figure 4 this test can be implemented in laboratories with good reproducibility so could be useful for all environmental matrices and for comparison of different leaching/extraction tests in order to make comparable the analytical results obtained with different methods. It could be also used to compare different sample to assess similarities in leaching behaviour. This last aspect could be very useful when for example a contaminated sediment is supposed to be a waste for land-filling management purposes. In this case if the pH-stat curve of the sample resemble the pH-stat curve of another waste already studied, we could reasonably affirm that it will be affected by the same solubility processes controlling leaching.

Submitted on invitation. Accepted on 3 June 2008.

References