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Environmental Toxicity Testing in the Risk Assessment of a Metal Contaminated Abandoned Mining Site in Hungary

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Abstract: A three tiered, iterative Environmental Risk Assessment methodology, including preliminary Qualitative Risk Assessment, Quantitative Hazard Assessment and Site Specific Quantitative Risk Assessment, was established to assess the environmental risk of point and diffuse pollution of mining origin at catchment scale [1]. The model site was an abandoned Pb and Zn sulphide ore mine in Gyöngyösoroszi, Toka-valley, NE Hungary [2]. The Integrated Risk Model considers the sources identified by the GIS-based (Geographical Information System) pollution map, the transport routes shown by the GIS-based flow accumulation model and the receptors of different land uses in the catchment. The site-specific quantitative risk was characterised by the Soil Testing Triad [3]. The three elements of the Triad are: physico-chemical analyses of the soil and the contaminants, the biological characterisation and ecotoxicity testing of the contaminated soil, measuring the response of single species in laboratory bioassays, the natural response of the soil microflora and plants or the dynamic response of the whole soil in microcosms. The Triad approach strongly supports the characterisation of the site specific risk as well as the selection and planning of the suitable remediation option.

Introduction

Risk Assessment (RA) is a technique by which the actual or potential adverse effects on ecosystem and humans can be predicted in a systematic fashion. This will enable to make decisions about managing the risk of contaminated sites of concern.

The developed tiered risk characterisation methodology is part of a complex risk management approach worked out to catchments polluted by point and diffuse contaminant sources. The main pollutants at our model site are Cd, Zn, Pb, As, emitted from mine technologies and wastes: primary sources like acidic mine drainage, lime precipitate, mine waste dumps, tailings dump and the secondary sources like sediments of reservoirs and creeks. The conceptual model has shown that the main risk is due to mobile metals, and metal mobilising processes, that is why the Environmental Risk Management focuses on the transport pathways, including plant-uptake of Cd and Zn.

Objectives

The objective was to develop, as part of the GIS-based Environmental Risk Management approach, a tiered, iterative Environmental Risk Assessment method for the qualitative and quantitative characterization of the risk on the basis of hazardous emissions from point and diffuse sources and to characterise the site specific risk by an integrated methodology: the Soil Testing Triad to identify the most risky sources and processes, the mobilisation and transport of toxic metals and to select the sustainable remediation solutions for point and diffuse sources.

Methodology and concept

The tiered GIS-based risk assessment methodology is based on the integrated risk model that integrates the Transport and the Exposure model and provides the basic concept of risk assessment. It follows the pathway from the pollution source through the polluted environmental element and its users, namely the receptors. The Integrated Risk Model was the uniform basis of the various level risk assessments, the qualitative, the generic and the site specific ones, and it was applied both to point and diffuse pollution sources as well as to the whole catchment [1].

Identification of the main hazard of the catchment showed that the risk of the mobilisation of metals, like Cd and Zn has primary importance and the transport to surface water and to plant endangers ecosystem and humans. Eroded solid waste endangers surface waters (by partition) and soil (by floods). The conceptual box model of the site (Fig 1) is the basic tool of the risk management of the catchment. It shows the input and output material fluxes. The GIS-based flow accumulation model is calibrated by the water balance. Pollutant transport from the sources is calculated from the water flux and emission parameters of the source-specific natural processes, like weathering, leaching and partition between soil phases.

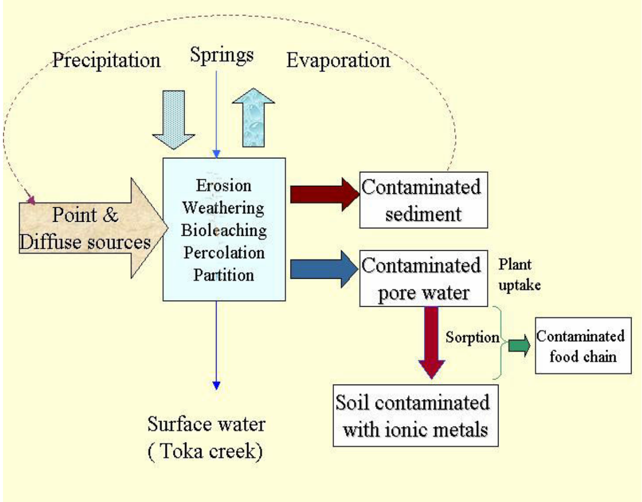

Figure 1 Conceptual model of the Toka area

Three-tiered Environmental Risk Assessment methodology

The three tiers of the Environmental Risk Assessment are: 1. Qualitative risk assessment 2. GIS-based Quantitative Hazard (Generic Risk) Assessment 3. Site specific Quantitative Risk Assessment.

For Qualitative Risk Assessment a site-specific score system was applied, resulting in a relative risk value for priority setting and preliminary ranking of pollution sources.

The Quantitative Hazard Assessment of point and diffuse sources was done by the GIS-based calculation of the metal emission from disposal sites of various size, sub-areas of point and diffuse sources and the total catchment area. The GIS-based environmental risk assessment starts from the individual mine waste dump level and is able to determine the hazard of the point sources, treating them as small individual water catchments. The quantitative emission data for sub-sites or any selected area were used for more precise ranking, for differentiation between point and diffuse sources and also for the estimation of the metal load on the watershed. The present risk on the Toka creek, the outflow of the catchment, is due to the total emission from all of the sources. By the elimination of any of the sources or by the reduction of their emission we can simulate the results of the remediation and predict its effect on the Toka-water.

The site specific Risk is due to the adverse effect of the wastes and polluted environmental elements on the users of the site, its waters, soils and plants. To characterize the site-specific risk two solutions are available: ***1. Direct measurement of the effect*** on the waters, sediments and soils of the site by toxicity assays [4] or ecosystem assessments [5]; **2. *The calculation of the Risk Quotient*** (RQ = PEC/PNEC = the ratio of the Predicted Environmental Concentration and the Predicted No Effect Concentration), predicting the contaminant concentration from measured data and comparing it to generic or site specific No Effect data, e.g. limit values or other environmental quality criteria.

Calculation of PEC from measured concentrations and the comparison of this value to the use-specific quality criteria is a good solution for surface waters or subsurface water-bases, but the solid phase containing environmental elements, the soil and sediment, are more complicate structures, than the water. The effect of their metal pollution depends on many factors, like the chemical form, the mobility and bioavailability of the toxic metals, the characteristics of the soil and the combinations of interactions between the elements of the soil matrix, the components of the pollution and the members of the soil biota. To predict the effect and the risk from the metal content measured (after extraction) by physico-chemical analytical methods – even if it is a sophisticated one, e.g. sequential extraction – brings poor results. Direct effect testing of soil and sediment gives more risk-relevant and environment-relevant result. The integrated evaluation of the physico-chemical, biological and toxicity test (Soil Testing Triad) allows a more detailed and dynamic conclusion of the risk. From the results of the Soil Testing Triad, the most suitable remediation (risk reduction) method can be also selected and planned.

Application of the Soil Testing Triad and toxicity testing

To characterize the risk of soils, wastes and sediments, the application of the Soil Testing Triad is demonstrated on some examples, showing how the integrated assessment improves the quality of information on toxic metals risk, increasing or decreasing mobility, the possible transport of the metals into the surface water and the availability for living organisms. The integrated evaluation of the traditional chemical analytics and the site-specific biological response gives an insight into the black box of the soil (and solid wastes) and makes possible a more dynamic testing and evaluation of natural and provoked risk-modifying processes [8]. In case of dynamic testing the consequences of an intervention on the "steady state" soil is followed in microcosms. The rate and type of the response of the soil and the dynamics of the process gives information on the biological status, adaptive potential, stability, biological and genetic flexibility of the soil biota and is able to predict the effect of the remediation technology. Some risk-related results of the application of the Soil Testing Triad [3] are introduced below.

Toxicity screening by rapid laboratory bioassays: a direct contact soil test with a self isolated *Bacillus subtilis* strain [4] and a direct contact luminescence inhibition test with *Vibrio fischeri*, the widely used luminobacterium were applied. The results made possible to identify the sources and prepare the first toxicity map of the catchment. One of the most risky transport pathways was identified: the contaminated sediment disposal by floods onto the soil of the agricultural land of the village [7].

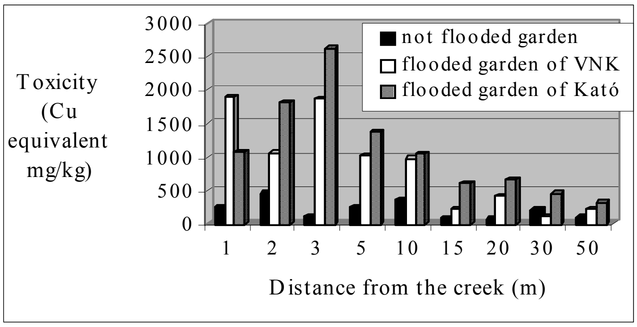

Figure 2 Toxicity of the soil of two flooded gardens (VNK and Kató)

Direct contact toxicity is a good indicator of mobility and bioavailability of the contaminants. The same metal concentration results in much higher plant toxicity on sandy, than in loamy soil, as it is shown in Figure 3. Lower mobility means lower risk, it can be the basis of some natural risk reducing processes and of the remediation by chemical and phytostabilisation.

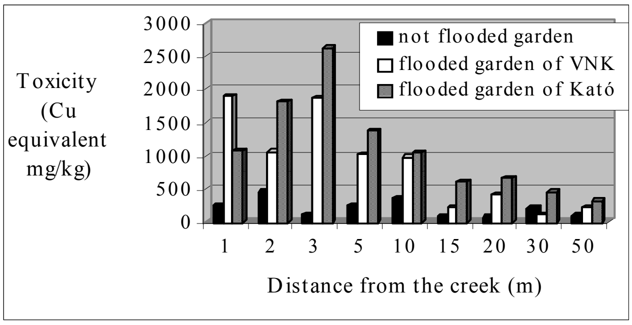

Figure 3 Influence of soil type on plant toxicity

Plant toxicity and extractable metal content correlate in those gardens which are flooded from year to year by the same pollutant, but do not correlate where the soil is polluted with wastes of different type and age. In the latter case (Figure 4b), some samples with high metal-content are not toxic, but some others with lower metal content show toxicity. Comparing the morphology and age of the polluting waste we could differentiate between freshly disposed and weathered wastes.

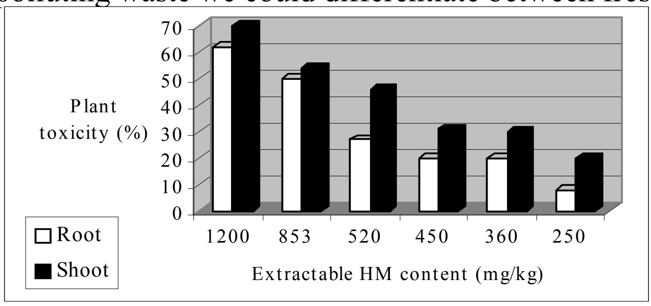

Figure 4a Toxicity of homogeneous pollutant

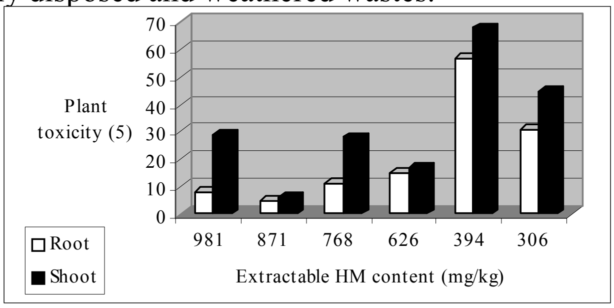

Figure 4b Toxicity of heterogeneous pollutant

Chemical time-bomb fate of the flotation tailings was shown by the integrated testing: it does not show toxicity on bacteria and plant, in spite of its extremely high metal content. The covering soil of low metal content due to direct contact with the waste became highly toxic for all testorganisms. The waste with its immobile metal content is highly risky when mixed to living soil and exposed to humidity, low pH and other environmental effects enhancing weathering (see table below).

Samples from the tailings dump	pH	Total metal (mg/kg) (Aqua Regia extract)			Soluble metal (mg/kg) (diluted nitric acid extract)			Bacterial toxicity	Plant toxicity
		Zn	Pb	Cu	Zn	Pb	Cu		
Deep layer, grey	7.0	31 858	4 971	2450	3.4	1.2	0.6	non toxic	non-toxic
Deep layer, red	7.1	2 248	481	114	4.3	0.1	0.0	non toxic	slightly toxic
Deep layer, yellow	7.3	7 571	2 766	984	3.9	1.7	0.6	non toxic	slightly toxic
Cover soil	4.7	603	186	72	42.2	1.9	0.5	very toxic	toxic

In leaching microcosms the complex leaching of sulphide mine waste was long-term studied. The emission from typical wastes was quantified and the mass balance used for risk assessment.

Soil microcosms were applied for studying ***chemical stabilisation*** of mine waste and contaminated soil using eight different stabilising agents. Soil Testing Triad was used for monitoring: a 4-step extraction and ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy), toxicity testing with organisms of 3 trophic levels and plant bioaccumulation test, to follow mobility of the metals. Reduction in the mobility of Cd and Zn was the most efficient with fly ashes A and B: 99–99,9 % in the water extract and 60–80 % in plant uptake.

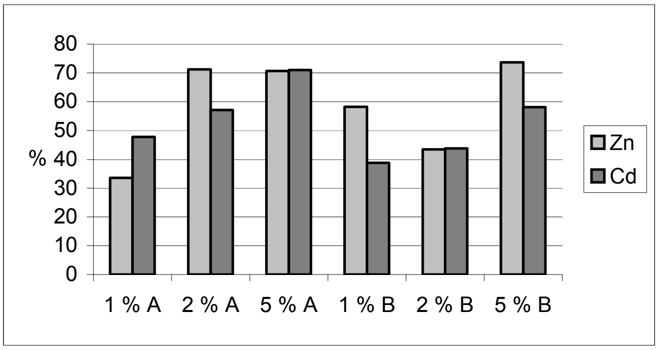

Figure 5 Decrease in Zn and Cd uptake in plant shoot

Conclusions

The tiered approach enabled setting of priorities amongst the pollution sources, differentiation between point and diffuse sources, hazard assessment for any sub-area, quantitative risk assessment, planning the scale of risk reduction and remediation. The Soil Testing Triad, including toxicity testing makes possible to characterise actual adverse effects on the members of the ecosystem. The response of soil living organisms is related to mobility and bioavailability of the contaminant in the soil. Integrating effect-assessment we can identify the chemical time bomb fate of the pollution and predict the risk reduction capacity of the soil and the efficiency of the remediation technology. From microcosm-results parameters for risk assessment and remediation planning can be obtained.

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