DEFINITION OF THE INTERVENTION LEVELS (LAW OF WASTES 10/1998, OF 21 APRIL) FOR CONTAMINATED SOIL IN THE GUADIAMAR RIVER BASIN (SPAIN) AND THE SITUATION OF THE SOIL AFTER THE REMOVAL OF THE MINE TAILINGS

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ABSTRACT

The recent Waste Law (Ley de Residuos 10/1998) establishes that the Autonomous Regions of Spain are required to declare a land that is contaminated with respect to the criteria, standards, etc, established by the Spanish Central Government.

Based on the natural background values for heavy metals in the Agrio and Guadiamar river basins, EMGRISA, on behalf of the Confederación Hidrográfica del Guadalquivir and the Consejería de Medio Ambiente de la Junta de Andalucía, jointly established the levels of intervention for heavy metals. This served as a reference for the declaration of contaminated ground as stipulated by the aforementioned law.

In order to determine the background values for heavy metals, a sampling campaign was designed along the entire length of the river basin in the areas unaffected by the mine sludge. For each different lithological formation the concentrations of heavy metals was defined. The geology at the headwater end of the Agrio and Guadiamar river basins consists of a wide strip of pyrite whose influence on the concentrations of heavy metals on the rest of the river basins are significant. The soil samples for posterior chemical analyses were collected superficially and at depth through the use of a drilling rig.

INTRODUCTION

In the early morning of April 25, 1998 a severe rupture occurred in a tailings dam located in the Boliden-Apirsa mining facilities in Aznalcóllar (Seville).

The rupture of the tailings dam caused the discharge of approximately two million cubic metres of mine tailings and approximately three million cubic metres of water with high concentrations of dissolved metal, fundamentally Fe, Pb, Zn, As and Cu in the form of sulphides, produced as a result of the process of floatation of pyrite. The discharge occurred along the lengths of the River Agrio and the River Guadiamar, from the dam to the limits of the Doñana National Park in the zone denominated Entremuros (Figures 1 and 2). This discharge affected approximately 60 km (37 miles) of river course and plains occupying approximately 4600 Ha. An area of approximately 2600 Ha was directly occupied by the mine tailings, whereas the rest of the area was only affected by acidic water.

Figure 1. Localisation diagram of the affected zones by the Aznalcóllar mine tailings discharge.

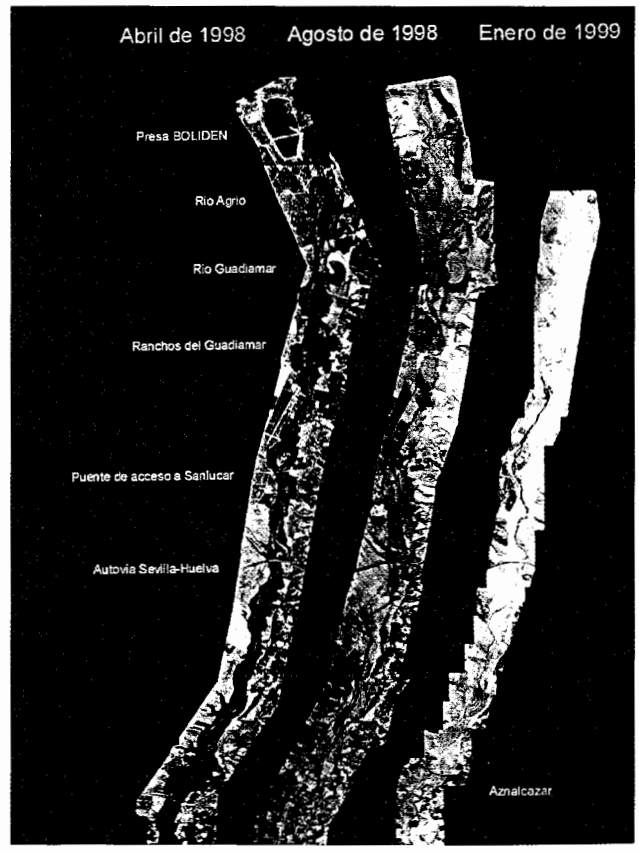

Figure 2. Aerial photography of the Guadiamar river.

The accumulation of heavy metals originating from the discharge along a major part of the Guadiamar river basin not only has affected the river course and banks but also the adjoining land. This has resulted in a loss of quality soil in the zone and the deterioration of nearly all of the hydraulic system (superficial water and aquifers).

In accordance and included in the Law of Waste (Law 10/1998, 21th April), the land belonging to the Guadiamar river basin could be considered as contaminated in accordance to Article 3 of the enforced Law: *"Contaminated land: all of those whose physical-chemical or biological characteristics have been negatively altered by the presence of components of a hazardous nature of human origin, in concentrations that may be a risk to human health or to the environment, in accordance to the criteria and standards which are determined by the Government.* Equally, in Article 27.1 establishes that the declaration of land that is contaminated corresponds to the Regional Autonomies, based on those criteria and quality standards that the Central Government establishes.

Due to the non-existence of national intervention levels and also due to the wide range in intervention levels existing both regionally and internationally, it was decided that it would be necessary to establish criteria and quality standards for soil in the Guadiamar river basin not affected by the tailings. In other words, soil located in the extreme limits of the Guadiamar river basin that was not directly or indirectly affected by the tailings discharge. The establishment of these criteria and quality standards permitted in the elaboration of an administrative Act to declare a zone as being contaminated as indicated in the Law of Waste 10/98.

The Confederación Hidrográfica del Guadalquivir, as an organism belonging to the Ministry of the Environment, was to whom it corresponded in the establishing of the criteria and quality standards, and contracted the company Empresa de Residuos Industriales, Sociedad Estatal (EMGRISA) in order to define the soil quality values.

The objective was the establishment of the original background levels of the river basin. This enabled to qualify those zones that were affected by the discharge of the mine tailings from Aznalcóllar as land being contaminated from land not contaminated. As the Guadiamar river basin was affected by an increase in the concentrations of heavy metals two levels were established:

- Reference levels (concentrations below which there are no risks); and
- Intervention levels (maximum allowable risk).

After the removal of the tailings affected by the discharge from the Aznalcóllar mine from the land along the river course and its proximity, EMGRISA completed in January 1999, on

behalf of the Confederación Hidrográfica del Guadalquivir, the "Preliminary characterisation of soils in the affected zone of the course of the River Guadiamar". The objective was to determine the zones which were to form in a larger sampling campaign in order to define with more precision both characteristics and concentrations.

As a complementary campaign, a second round of sampling was completed in March 1999, on behalf of the Junta de Andalucía (Government of Andalusia), in which 969 soil samples were collected.

The results of the concentrations of heavy metals were compared the intervention levels established by the Junta de Andalucía and presented on the maps of *"Levels of residual contamination in banks and slopes"* and *"Levels of residual contamination in the river course"*. Both were included in the Balance of Actions Report from the Junta de Andalucía and the Ministry of the Environment.

PREVIOUS STUDIES

In any type of investigation it is necessary to complete a desktop study in order to obtain the information, which will aid in the design of the field campaign. In this case information consulted included cartographic maps, soil, geological, geochemical, hydrological studies, etc. and human activities such as previous sampling campaigns and analyses.

In additional, information was collated on existing regulations on soil contamination at international, national and autonomic level. The soil quality standards of the countries that were advanced in the legislative process were analysed because their experience would be of great help in the moment of establishing corresponding limits for the study zone. The countries whose standards were consulted were Belgium, Canada, Denmark, Finland, Holland, Germany, Italy, Sweden, Switzerland, United Kingdom, and U.S.A.

At national level the existing regulation is included in the Law 10/1998 of April 21 on Waste. At the present moment the Central Government is working on defining the soil and ground water quality standards, however, they are still being developed.

At autonomic level there are three regions that have elaborated and published proposed soil quality standards and they are Galicia, Catalunya and the Basque Country.

FIELD WORK

After digesting and analysing the obtained information, the design of the sampling campaign to determine the background levels was completed using random sampling points in the area always outside the zone of affection. The soil samples were collected both upstream of the rivers Agrio and Los Frailes and downstream to the confluence of the River Guadiamar and in each different geological formation encountered. In addition a soil boring campaign was designed in order to study deeper both in the geological and hydrogeological study of the zone.

The total number of samples collected in this phase of work were 376, spread in the following zones (Figure 3):

- Upstream of the River Agrio drainage basin until the decantation dam (24); and
- Los Frailes stream drainage basin until the dam and affected zone (Guadiamar y downstream of the River Agrio drainage basin (352).

This campaign was completed with the analytical results from the sampling completed by the Consejería de Agricultura y Pesca (135 samples), and with 38 more completed by the Instituto Tecnológico Geominero de España (ITGE).

In the diverse campaigns for soil characterisation the sampling points were randomly spread always in the area within the affected zone.

The total number of samples collected were 1592 of which 1290 were superficial.

ANALYTICAL DETERMINATION

Of the total number of samples collected by EMGRISA to determine background levels, 311 samples were selected for analyses. The parameters analysed for were heavy metal (As, Ba, Cd, Cr, Co, Cu, Pb, Ni, Zn, Mn and Mo) and pH. In addition, in 70 samples the organic matter content and % of clay were determined.

In the diverse sampling campaigns for soil characterisation in the affected zone the samples were analysed for As, Cd, Cu, Pb and Zn. In additional, in some of the samples C, N, carbonates, pH, moisture content and particle size analysis were determined.

The preparation of the sampled for their chemical-physical analyses was completed in accordance to ISO 11464. The techniques and methods for determination used are described on Table 1.

STATISTICAL TREATMENT OF THE DATA IN ORDER TO DETERMINE THE BACKGROUND VALUES

In the moment of treating statistically the results obtained, those values, which presented anomalies in some of the parameters analysed for, were excluded from the rest of the data. In addition, in three of the metals analysed for (Ba, Cd y Mo), the majority of the results (76% for Ba, 92% for Cd and 93% for Mo) were below the method detection limits. As a result, these metals were not considered in the establishment of the soil concentration background values.

In addition, in the group of samples analysed, those samples collected upstream of the River Agrio drainage basin (north of the tailings dam) were separated and subjected to an independent statistical analysis. The rest of the samples obtained and analysed by EMGRISA were divided into distinct subgroups in order to establish if there existed significant variations in the values obtained in function of both lithology and depth of soil sample collection.

Determination	pH	Metals	Organic matter	Clay
Method	• ISO/DIS 10390 • Official Method of Analysis. Ministry of Agriculture, Food and Fisheries (1986).	• ISO/DIS 11466 • EPA 6010 • EPA 7471	Official Method of Analysis. Ministry of Agriculture, Food and Fisheries (1986)	
Technique	Electrometer	Spectrometry of Plasma Emissions ICP	Volumetric Valuation	Sieve analysis and laser

Table 1. Analytical methods and techniques

Statistical analysis and establishment of the background values

Less than twenty values were presented in some of the subgroups studied, by which the statistical analysis for them is either not recommended or not representative. In addition, the data obtained from the rest of the subgroups did not vary significantly form one and another. As a result it was decided to utilise the values corresponding to the superficial level, which are not only the more representative but also because of the potential repercussion on the population who would be in direct contact with the land. Of the values obtained from the superficial soil samples the results obtained by the 38 soil samples collected by the Instituto Tecnológico Geominero de España (ITGE) were also included.

In order to complete a coherent statistical analysis, the lost values (that is, those below the method detection limit) may not be considered as such (either eliminating them or substituting of a determined value). It is more correct, statistically speaking, to generate for each component a percentage of probable values below the method detection limit and discard the rest.

On another part, transformations were made in some of the variables that permitted the obtention of normal distributions. This permitted the treatment of data in a statistical context with an additional guarantee for the use of an adequate known statistical model in order to make inferences on the parameters. It is not precise to insist that this is the habitual methodology applied in the statistics.

The transformations utilised for normality were the usual Box-Cox family, which in this case were by transformation by natural logarithms and transformation of potentials both without a scaling factor. In continuation these were contrasted with the normality of the variable transformations of Kolmogorov-Smirnov, observing the associated p-value.

Upon these transformed variables which adjusted to a normal distribution, a statistical analysis was completed as a function and in order to establish the background values, it was considered in all of the cases the value of the 95 percentile (recalculating the inverse of the transformation made in each case). The exceptions were for Mn and Cr, which were bimodal variables and cannot suffer any transformation and in which they were considered the value of $\bar{x}+2\delta$, where $\bar{x}$ are the arithmetic mean and δ is the standard deviation.

On another side, the possible correlation of the diverse metals with clay content, organic matter and pH were studied. The correlation was of minor significance between pH and organic matter and metals, basically because there were little variables, which could be compared to in detail.

However, in terms of linear regression formula between organic matter, pH and clay, it was not apparent to deduce in any of the regression conducted except for perhaps Mn, however, with a low viability (baring in mind that the variable for Mn is not normal), and for Ni and especially Zn, but the values have to be considered with care.

Standards for Guadiamar river drainage basin

In function of the statistical analysis completed the background values were established (Table 2).

	As	Cr	Co	Cu	Pb	Ni	Zn	Mn
Background Values	52	90	16	120	86	39	366	1043

Table 2. Background levels.

Based on the completed study and in accordance to the Law 10/1998, the intervention levels were proposed for the Guadiamar river drainage basin (Tables 3 and 4).

As	Cu	Pb	Zn	Cd
100	500	500	1200	10

Table 3. Intervention levels (mg/kg). Zones of non-sensitive use.

As	Cu	Pb	Zn	Cd
52	250	350	700	5

Table 4. Intervention levels (mg/kg). Zones of sensitive use.

These levels have been accepted and approved by the Consejería de Medio Ambiente de la Junta de Andalucía in the Order of 18 of December, 1998 in which are fixed the concentration limits for soils affected by the Aznalcóllar mine accident.

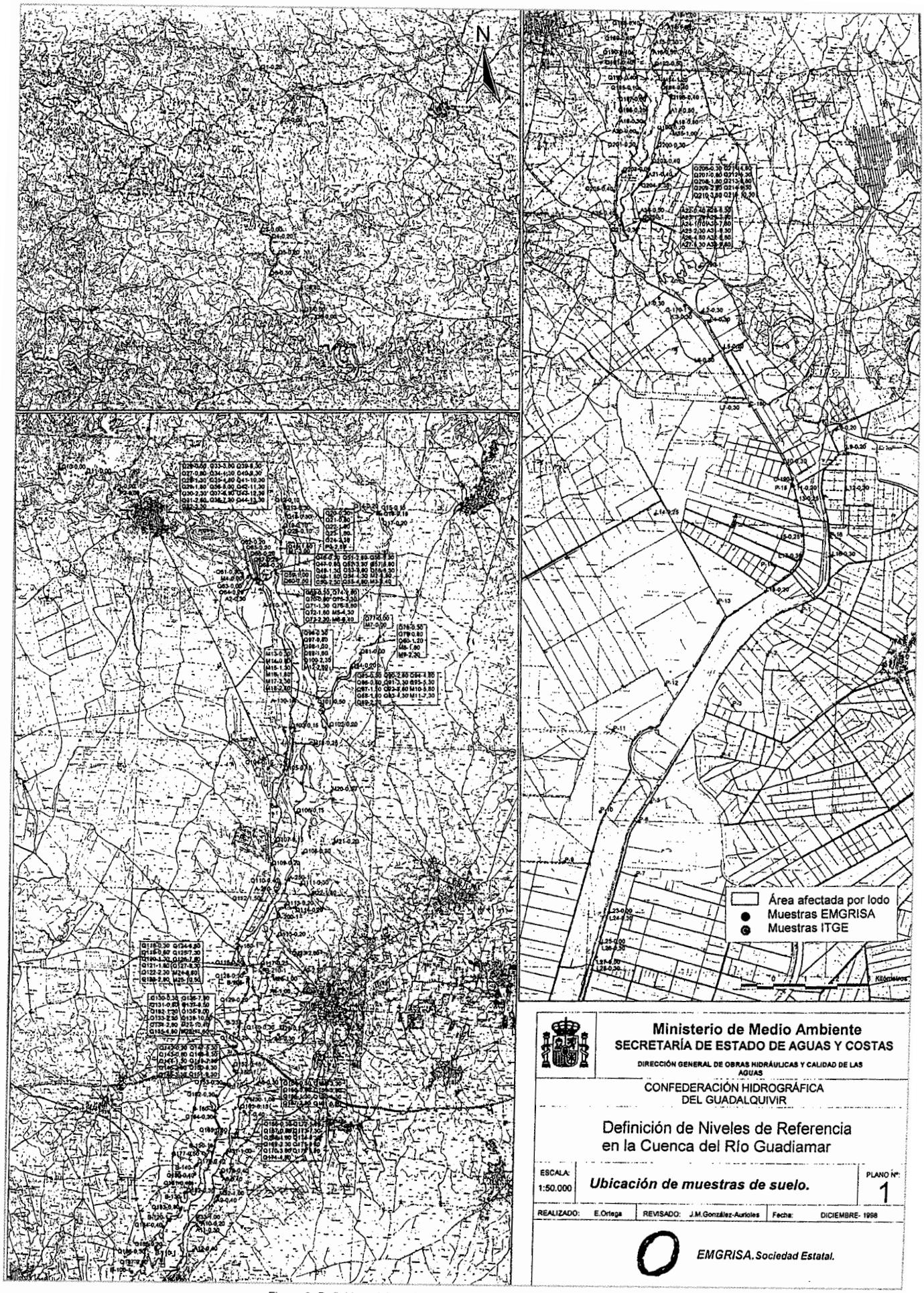

Figure 3. Definition of the reference levels in the Guadiamar river basin.

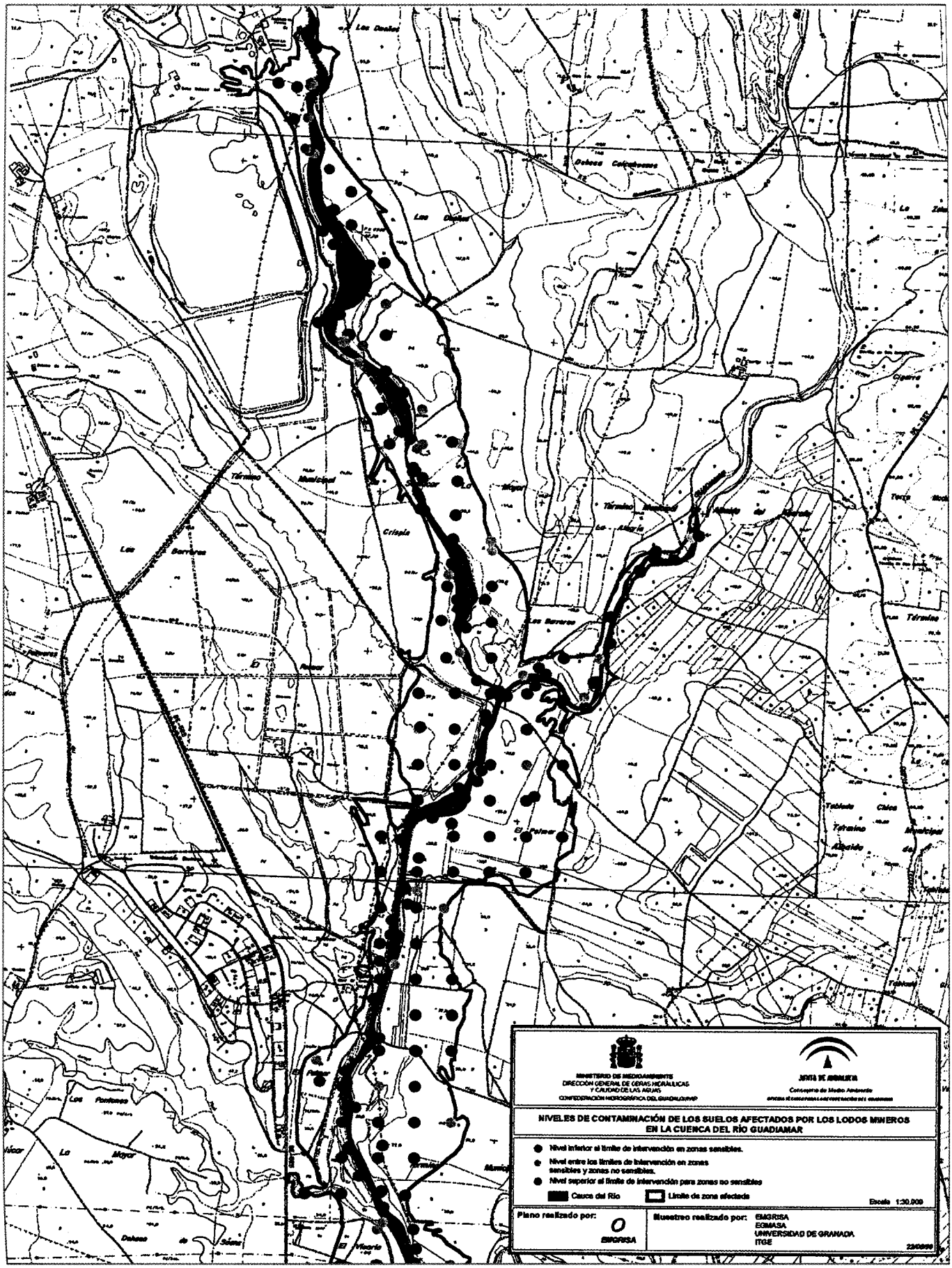

Figure 4. Contamination levels of the affected land by the mine tailings in the Guadiamar river basin.

SITUATION OF THE SOIL AFTER THE REMOVAL OF THE MINE TAILINGS

The results obtained by the diverse soil sampling campaigns completed in the affected zone by the different organisms, EMGRISA completed in June 1999 an integrated plan of the results obtained (Figure 4).

The Table 5 summarises the number of soil samples collected and analysed by each of the different organisms implicated.

In the Table 6 a summary interpretation of the results obtained comparing them to the intervention levels established by the Order of December 18, 1998 by the Junta de Andalucía is enclosed.

Organisms	Soil samples collected	Samples analysed
EMGRISA	408	1277
EGMASA	869	-
ITGE	48	48
GRANADA UNIV.	267	267
Total	1592	1595

Table 5. Soil samples collected and analysed.

		All samples (1592)						Superficial samples (1290)					
		As	Cd	Cu	Pb	Zn	Total	As	Cd	Cu	Pb	Zn	Total
Samples with values inferior to the level of intervention in sensitive zones	No samples	875	1297	1240	1250	948	663	686	1025	986	982	721	500
	%	55	81	78	79	60	42	53	79	76	76	56	39
Samples with values in between the levels of intervention in sensitive and non-sensitive zones	No Samples	256	245	276	114	300	341	196	219	240	97	262	279
	%	16	15	17	7	19	21	15	17	19	8	20	22
Samples with values superior to the levels of intervention in non-sensitive zones	No Samples	461	50	76	228	344	588	408	46	64	211	307	511
	%	29	3	5	14	22	37	32	4	5	16	24	40

Table 6. Results of the soil samples collected in the affected zone by mine tailings in the river Guadiamar drainage basin.