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title: **Proposed procedure to evaluate the chemical status of groundwater bodies**

author(s): **Damián Sanchez-García**
University of Málaga, Spain, dsanchez@uma.es

Francisco Carrasco-Cantos
University of Málaga, Spain, fcarrasco@uma.es

Iñaki Vadillo-Pérez
University of Málaga, Spain, Vadillo@uma.es

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INTRODUCTION

According to Article 5 of the water framework directive (WFD, European Commission, 2000) all member states are required to conduct a study determining the impact of human activity on the status of groundwater. In accordance with the deadlines defined in the WFD, the first analysis of pressures and impacts was to be completed in December 2004. This analysis of pressures and impacts should be reviewed and updated in each European river basin district by December 2013, and thereafter every six years.

The aim of this work is to propose a procedure to evaluate the impact on the chemical status of groundwater bodies, which may be a procedure to be used in the review to be completed in 2013 in all European river basins.

ENVIRONMENTAL OBJECTIVES

Preliminary considerations

An impact occurs when a given body of water fails to meet the environmental objectives that the directive sets out in Article 4. This leads to the conclusion that as a preliminary step towards the identification of impacts on the chemical status of groundwater bodies, it is necessary to review the environmental objectives of groundwater bodies.

Groundwater bodies

The objective that the WFD establishes for groundwater bodies is to achieve a good chemical and a good quantitative status by 2015. The parameters that should be used to evaluate the chemical status of groundwater bodies are electrical conductivity and the concentration of pollutants (Tab. 1).

Table 1. Definition of good groundwater chemical status according to the WFD.

Objective	Parameters	Criteria	Reference
Good chemical status	Conductivity	Not indicative of saline or other intrusion	Annex V, section 2.3
	Concentration of pollutants	Do not exhibit the effects of saline or other intrusions	
		Do not exceed the quality standards applicable under Directive 2006/118/EC	
		Do not result in failure to achieve the environmental objectives nor any significant diminution of quality of associated surface waters	

In order to achieve good chemical status, the electrical conductivity must not indicate the existence of salinisation or other types of intrusions, and concentrations of pollutants must be below the quality standards (maximum permissible concentrations) established in Directive 2006/118/EC (Groundwater Directive, European Commission, 2006). Furthermore, the chemical and ecological status of surface water bodies and ecosystems that directly depend on the groundwater body should not be deteriorated (Tab. 1).

PROPOSED PROCEDURE TO EVALUATE IMPACTS ON GROUNDWATER CHEMICAL STATUS

Background

The documents of reference that have been used to establish this methodology are the following: water framework directive, guidance document nº 3 on the analysis of pressures and impacts (European Commission, 2003) and the manual for the identification of pressures and analysis of impacts on surface waters, drawn up by the Spanish Ministry of the Environment (2005, unpublished data).

The objective of an impact assessment on the chemical status is to identify all the chemical substances or physicochemical parameters that can cause a groundwater body to not meet its environmental objectives. Therefore, the list of pollutants and indicator parameters considered to assess impacts should be as extended as possible.

Impact classes proposed

Two types of impacts are proposed in this work: an *important* impact and a *slight* impact. Consequently, the result of an impact assessment may be one of the following four options: a) *important* impact, b) *slight* impact, c) *no impacts reported* and d) *no data found*.

An *important* impact will be present when one of the parameters used to assess the chemical status does not meet the quality standard. The *slight* impact is reserved for those cases which do not exceed the quality standard, however the concentration or value of the parameter considered indicates that the natural status of a water body has been altered due to human activity. If neither of these cases applies, the water body will be defined as *no impacts reported*, and where no data is available for evaluation, the classification *no data found* will be assigned.

Impact assessment on the chemical status of groundwater bodies

The requirements for a groundwater body to have a good chemical status can be summarised into the following:

- 1. No evidence exists of salinisation or seawater intrusion.
- 2.The concentrations of contaminants do not exceed the quality standards set in the Groundwater Directive (Directive 2006/118/EC).
- 3. The chemical or ecological status of surface water bodies and terrestrial ecosystems that depend on these groundwater bodies do not deteriorate.

Table 2. Parameters and criteria for assessing the impacts on the chemical status of groundwater bodies. (All concentrations are expressed in µg/l unless otherwise indicated).

	Impact				Impact		
Parameter	**Slight**	**Important**		**Parameter**	**Slight**	**Important**	
1. Electrical conductivity	Upward temporary evolutions			(d) Benzo(g,h,i)-perylene	Presence	MA: Σ>0.002	
2. Chloride				(e) Indeno(1,2,3-cd)-pyrene			
3. Sodium				35. Simazine	Presence	MA>1	>4
4. Sulphate				36. Tributyltin compounds	Presence	MA>0.0002	>0.0015
5. Nitrates	20-50 mg/l	>50 mg/l		37. Trichloro-benzene	Presence	MA>0.4	
6. Pesticides	Presence	>0.1 (indiv.)	>0.5 (total)	38. Trichloro-methane	Presence	MA>2.5	
7. Alachlor	Presence	MA>0.3	>0.7	39. Trifluralin	Presence	MA>0.03	
8. Anthracene	Presence	MA>0.1	>0.4	40. (a) Total DDT	Presence	MA>0.025	
9. Atrazine	Presence	MA>0.6	>2.0	(b) P,p-DDT	Presence	MA>0.01	
10. Benzene	Presence	MA>10	>50	41. Aldrin	Presence	MA: Σ>0.01	
11. Brominated diphenylether	Presence	MA>0.0005		42. Dieldrin			
12. Cadmium: <40 mg/l CaCO3	-	MA>0.08	>0.45	43. Endrin			
40-50 mg/l CaCO3	Presence	MA>0.08	>0.45	44. Isodrin			
50-100 mg/l CaCO3	>0.45	MA>0.09	>0.60	45. Carbon tetrachloride	Presence	MA>12	
100-200 mg/l CaCO3	>0.60	MA>0.15	>0.90	46. Tetrachloro-ethylene	Presence	MA>10	
≥200 mg/l CaCO3	>0.90	MA>0.25	>1.50	47. Trichloro-ethylene	Presence	MA>10	
13. C10-13 Chloroalkanes	Presence	MA>0.4	>1.4	48. Chloro-benzene	Presence	MA>20	
14. Chlorfenvinphos	Presence	MA>0.1	>0.3	49. Dichloro-benzene	Presence	MA>20	
15. Chlorpyrifos	Presence	MA>0.03	>0.10	50. Ethyl-benzene	Presence	MA>30	
16. 1,2-Dichloroethane	Presence	MA>10		51. Metolachlor	Presence	MA>1	
17. Dichloromethane	Presence	MA>20		52. Terbuthylazine	Presence	MA>1	
18. Di(2-ethylhexyl)-phthalate	Presence	MA>1.3		53. Toluene	Presence	MA>50	
19. Diuron	Presence	MA>0.2	>1.8	54. 1,1,1-Trichloro-ethane	Presence	MA>100	
20. Endosulfan	Presence	MA>0.005	>0.010	55. Xilene	Presence	MA>30	
21. Fluoranthene	Presence	MA>0.1	>1.0	56. Cyanides	Presence	MA>40	
22. Hexachloro-benzene	Presence	MA>0.01	>0.05	57. Fluoride	>1.0 mg/l	MA>1.7 mg/l	
23. Hexachloro-butadiene	Presence	MA>0.1	>0.6	58. Arsenic	10-50	MA>50	
24. Hexachloro-cyclohexane	Presence	MA>0.02	>0.04	59. Cupper: ≤10 mg/l CaCO3	>2.5	MA>5	
25. Isoproturon	Presence	MA>0.3	>1.0	10-50 mg/l CaCO3	>11	MA>22	
26. Lead and its compounds	>10	MA>7.2		50-100 mg/l CaCO3	>20	MA>40	
27. Mercury	Presence	MA>0.05	>0.07	>100 mg/l CaCO3	>60	MA>120	
28. Naphthalene	Presence	MA>2.4		60. Total chromium	>10	MA>50	
29. Nickel and its compounds	>10	MA>20		61. Chromium VI	>1	MA>5	
30. Nonylphenol	Presence	MA>0.3	>2.0	62. Selenium	>1	MA>1	
31. Octylphenol	Presence	MA>0.1		63. Total zinc: ≤10 mg/l CaCO3	>6	MA>30	
32. Pentachloro-benzene	Presence	MA>0.007		10-50 mg/l CaCO3	>40	MA>200	
33. Pentachloro-phenol	Presence	MA>0.4	>1.0	50-100 mg/l CaCO3	>60	MA>300	
34. Polyaromatic hydrocarbons:				>100 mg/l CaCO3	>100	MA>500	
(a) Benzo(a)pyrene	Presence	MA>0.05	>0.10	64. Total phosphorus	>12	>50	
(b) Benzo(b)fluor-anthene	Presence	MA: Σ>0.03		65. Biological oxygen demand	>2.5 mg/l	>4.0 mg/l	
(c) Benzo(k)fluor-anthene				66. Ammonium	Presence	>0.5 mg/l	
				67. Phosphate	Presence	>0.5 mg/l	

"MA": mean annual concentration; the other values are expressed as maximum allowable concentrations

Table 2 shows the list of the 67 physicochemical parameters proposed in this work to identify the impacts on the chemical status of groundwater bodies, as well as the threshold values proposed to define the *slight* and *important* impacts.

Salinisation or seawater intrusion

Four physicochemical parameters are proposed to identify the existence of an impact made by salinisation or seawater intrusion (parameters 1 to 4 in Tab. 2): Electrical conductivity, Chloride concentration, Sodium concentration and Sulphate concentration.

The criteria proposed to identify an impact by salinisation or seawater intrusion are based on the existence of increasing trends over time with respect of any of these parameters. Given the

difficulty of establishing a single quantitative threshold to differentiate between the *important* and *slight* impacts, a distinction based on the following characteristics of increasing trends is proposed: number of control points showing an upward trend, number of physicochemical parameters showing an upward trend and clarity or evidence of trends.

Quality standards established in Directive 2006/118/EC

Two quality standards are established in Annex I of this directive related to the concentration of nitrate (50 mg/l) and pesticides (0.1 µg/l for a single pesticide and 0.5 µg/l for the sum of pesticides). These quality standards are proposed to identify the existence of an *important* impact given that going over this limit would imply that a groundwater body fails to reach the good chemical status (5 and 6 in Tab. 2). Furthermore, it is necessary to define another threshold value to identify the existence of a *slight* impact. In the case of nitrate, a compound that can be found naturally in water, it is proposed to define a *slight* impact when the concentration is between 20 and 50 mg/l. With respect to pesticides, which are substances that do not come from natural sources, it was decided to consider its mere existence in water as evidence of a *slight* impact.

Surface water bodies and associated ecosystems

One of the requirements of the WFD for a groundwater body to have a good chemical status is that the status of associated surface water bodies and dependent ecosystems does not deteriorate by its action.

Many groundwater bodies have been defined in aquifers that discharge through one or more springs that in many cases feed rivers and lakes, which, in turn, can constitute surface water bodies. Consequently, a deterioration in the status of this groundwater would result in a deterioration of the quality of surface water bodies and associated ecosystems. For this reason, it was considered necessary to include in the list of parameters used to assess the chemical status of groundwater bodies, those parameters which are necessary to evaluate the chemical status of surface waters. These substances are numbered from 7 to 65 in Tab. 2.

The parameters 7 to 47 in Tab. 2 were obtained from the Directive 2008/105/EC on environmental quality standards in surface waters (European Commission, 2008), which defines quality standards that set maximum permissible concentrations allowed in surface water for 41 substances. These maximum concentrations or quality standards are expressed in two different manners: as average annual values and as maximum allowable concentrations. In this proposal, surpassing these concentrations is considered as evidence of an *important* impact since they will prevent an associated surface water body to reach a good chemical status.

In regards to *slight* impacts, the 41 substances have been grouped into two types: those that are not naturally found in water (all of them except for cadmium, lead and nickel), and those that can originate from both natural sources as well as polluting activities. In regards to those not naturally found in water, it was decided that their mere presence in water is indicative of a *slight* impact, and with respect to cadmium, lead and nickel (numbers 12, 26 and 29 respectively in Tab. 2), a *slight* impact is present when concentrations surpass 10 µg/l for lead and nickel, and 0 to 0.9 µg/l (depending on water hardness) for cadmium. In the case of lead, the value corresponds to the maximum concentration recommended by the World Health Organiza-

tion (after Baird, 1999), whilst values of nickel and cadmium have been established within the framework of this work as no previous information was found.

Substances from 48 to 63 in Tab. 2 were obtained from the Royal Decree 995/2000, of 2 June, which defined the quality objectives for certain pollutants (Official [Spanish] State Gazette, *BOE* No. 147, 20.6.2000). The maximum concentrations established in the Royal Decree have been interpreted as indicating the existence of an *important* impact. In regards the thresholds that identify the existence of a *slight* impact, its estimate is calculated using the following three criteria:

- For chemical substances that do not have a natural origin, their mere presence in the water reflects the existence of a *slight* impact (cells with the term "Presence" in Tab. 2).
- In the case of arsenic (number 58 in Tab. 2), which unlike the above substances can have a natural origin, the threshold considered was 10 µg/l which is the maximum concentration recommended by the World Health Organization (after Baird, 1999).
- Concentrations assigned to the parameters fluoride, copper, total chromium, chromium VI, selenium and zinc to detect a *slight* impact have been established within the framework of this work.

Finally, the substances 64 and 65 (total phosphorus and biological oxygen demand respectively) were obtained from Annex VIII of the WFD and thresholds considered were taken from the guidance document on the analysis of pressures and impacts elaborated by the European Commission (European Commission, 2003).

Other Pollutants

Ammonium and phosphate (parameters 66 and 67 in Tab. 2) are not included in the definition of good chemical status for groundwaters, however they can be found in other parts of the WFD (section 2.4.2 of Annex V and Annex VIII of the WFD). Therefore, both ammonium and phosphate have been considered in the list of parameters used to assess the chemical status of groundwater bodies.

Their mere presence in groundwater has been interpreted as indicative of a *slight* impact since they rarely have a natural origin, whereas concentrations greater than 0.5 mg/l are indicative of an *important* impact (value established within the framework of this work).

CONCLUSIONS

This work presents a methodology for assessing the impacts on the chemical status of groundwater bodies. The proposed procedure has been developed on the basis of the environmental objectives of the WFD for groundwater bodies. Following this, criteria based on a series of physicochemical parameters and threshold values were established, arising from their respective environmental objectives, from which the existence of an impact has been determined. Finally, two possible classifications to define the impact on groundwater have been established in function of their magnitude, *slight* and *important*.

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