Agricultural chemicals and its impact on the quality of water resources: the case of the Valley of Carrizo, Sinaloa, Mexico

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Abstract: The paper describes a study realized in the District of Irrigation 076 Valley of the Carrizo, which is located in the north part of Sinaloa's State. Politically, it includes departs from Ahome municipalities and The Fort, and geographically are located between the coordinates 26º 05', 26º 22' ' north latitude and 108º 53', 109º 00' of length west. It borders in the northern part on the State of Sonora, in the southern part on the Saw Western Mother and in the western part on the Gulf of California. The general aim of the study is determine the levels of pollution by pesticides and fertilizers in the superficial waters of the District of Irrigation 076 Valley of the Carrizo.

A hypothesis is that the rate of application of fertilizers and pesticides for maize growth exceeds the dose recommended by the National Institute of Forest, Agricultural and Cattle Investigations (INIFAP). Another hypothesis is that the superficial waters used in the District of Irrigation 076 Valley of the Carrizo are contaminated by fertilizers since it exceeds to a great extent the norm NOM-001-ECOL-1996 for the maximum permissible limits (LMP) of total nitrogen that is of 15 mg/L and on the other hand for the total phosphorus, which has as LMP 5 mg/L it is not exceeded in any point, as well as by some chemical components of pesticides used in the agriculture of the Valley.

The methodology applied to estimate the possible environmental impact of the pesticides in the water, was first determined which are those pesticides and fertilizers that are being used in the sowing of the maize, by means of the application of survey to producers.

For the monitoring of the superficial waters of drains collectors and the one discharged to the sea, we followed recommendations of the British Geological Survey (BGS), which coincide with the one of US-EPA and which are used by the Arizona Department of Enviromental Quality in the United States.

The method used for the analysis of pesticides was that of Gas chromatography and for the analysis of fertilizers the method NMX-AA-026-SCFI-2001 for N-total; NMX-AA-029-SCFI-2001 for P-total and, for nitrates and nitrites the method of brucina and reduction of cadmium.

The results of the survey on the use of fertilizers and pesticides in the region, determined that the dimetoato applies to himself in average 367.1 kg/ha. of nitrogen and 70.05 kg./ha. of phosphorus, the metamidofos, clorotalonil and glifosato, were the pesticides most used for maize growth. The following specific amount has been evaluated for 33,771.73 hectares of maize culture in the cycle autumn - winter 2007-2008.: dimetoato 1.25 lt/ha, metamidofos 1.85 lt/ha, clorotalonil 1.54 lt/ha and glifosato 1.87 lt/ha. Concentrations in superficial water show that nitrates exceed the LMP in all samples, according to the NOM-127-SSA1-1994; the LMP for nitrites has been exceeded in 16 samples and the total nitrogen in 15, of the total of 20.

The presence of high concentrations of nitrates and nitrites in the agricultural drains open channel collectors has been confirmed by chemical analyses. These contaminants can contribute to the pollution of the phreatic shallow water, and influence the quality of the water of irrigation, causing a risk for the health of the exposed population, as well as for the fishing activity.

Keywords: Valley of the Carrizo, fertilizers, Pollution of superficial waters.

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Riassunto: *L'articolo descrive uno studio realizzato nel Distretto di Irrigazione 076 nella Valle del Carrizo, ubicata nel Nord dello Stato di Sinaloa. Politicamente esso include parti della municipalità di Ahome e Il Fort, e geograficament e è situata tra le coordinate 26º 05', 26º 22' ' latitudine Nord e 108º 53', 109º 00' Est. Essa cinge a nord lo Stato di Sonora, a Sud la Saw Western Mother e a Ovest il Golfo di California Lo scopo dello studio è determinare il livello di inquinamento da pesticidi e fertilizzanti nelle acque superficiali nel distretto 076 della Valle del Carrizo.*

Un'ipotesi è che la quantità di fertilizzanti e pesticide usati per la crescita del mais sia superiore alla dose raccomandata dal National Institute of Forest Agricultural and Cattle Investigations (INIFAP). Un'altra ipotesi è che le acque superficiali usate nel Distretto di Irragazione 076 nella Valle del Carrizo siano contaminate dai fertilizzanti che eccedono in larga misura la norma NOM-001-ECOL-1996 per ciò che riguarda il limite massimo permesso (LMP) di azoto che è 15 mg/L ; mentre per quello che riguarda il fosforo, il cui limite è LMP 5 mg/L esso non viene superato in nessuna zona, come anche per altri componenti chimici di pesticidi usati nell'agricoltura della Valle La metodologia applicata per stimare il possibile impatto ambientale dei pesticidi nell'acqua fu in primo luogo l'individuazione dei tipi di pesticidi e fertilizzanti che vengono usati per la semina del mais, attraverso un'indagine presso i produttori.

Per il monitoraggio delle acque superficiali dei collettori di scolo e di quelle scaricate in mare, noi seguiamo le raccomandazioni del Servizio Geologico Britannico (BGS), che coincidono con quelle del US-EPA e che sono usate dal Dipartimento dell'Arizona sulla Qualità Ambientale negli Stati Uniti.

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Per il monitoraggio delle acque superficiali dei collettori di scolo e di quelle scaricate in mare, noi seguiamo le raccomandazioni del Servizio Geologico Britannico (BGS), che coincidono con quelle del US-EPA e che sono usate dal Dipartimento dell'Arizona della Qualità Ambientale, negli Stati Uniti.

Il metodo usato per l'analisi dei pesticidi è stato il Gas Cromatografo e per le analisi dei fertilizzanti il metodo NMX-AA-026-SCFI-2001 per N-totale; NMX- AA-029-SCFI-2001 per il P-Totale e per i nitrati e i nitriti il metodo di brucina e la riduzione del cadmio.

Il risultato dell'indagine sull'uso dei fertilizzanti e dei pesticidi nella regione ha stabilito che il dimetoato ha nella sua composizione in media 367.1 kg/ha di azoto e 70.05 kg/ha di fosforo, il metamidofo, il cloratonil e il glifosato sono i pesticidi più usati per la crescita del mais. Il seguente valore specifico è stato valutato per 33,771.73 ettari di coltura di mais nel ciclo autunno -inverno 2007-2008: dimetoato 1.25 lt/ha, metamidifo 1.85 lt/ha, cloratonil 1.54 lt/ha e glifosato 1.87 lt/ha. Le concentrazioni nelle acque superficiali mostrano che i nitrati superano il LMP in tutti gli esempi, in accordo con il NOM-127-SSA1-1994; il LMP per i nitriti è stato superato in 16 esempi e l'azoto totale in 15 dei 20 complessivi.

La presenza di alte concentranzioni di nitrati e nitriti nei collettori aperti di scolo è stata confermata dalle analisi chimiche. Questi contaminanti possono contribuire all'inquinamento della falda freatica, e influenzare la qualità dell'acqua per l'irrigazione, causando un rischio per la salute delle popolazioni esposte così come per l'attività della pesca.

Introduction

Environmental pollution is a serious global problem. When specifying the sources of water pollution, agriculture is increasingly more often prominent.

Currently, the excessive use of agrochemicals is a type of pollution that has begun to take a high importance as it is causing high concentrations of nitrites and nitrates in surface and ground waters (Gonzalez, 1990) and pesticide residues in surface waters and in discharges to the sea.

Sustainable agriculture is one of the biggest challenges. This sustainability implies that agriculture is not only able to ensure a sustained food supply, but their environmental, socioeconomic and health are recognized and addressed in national development plans.

It is well known that agriculture is the main user of freshwater resources as it uses a world average of 70 percent of all surface water supplies. With the exception of the water lost through evapotranspiration, the water used in agriculture is recycled back into shape and surface water or groundwater. However, agriculture is both responsible and victim of the pollution of water resources. It is responsible because of the discharge of pollutants and sediments into surface waters and / or groundwater, the net loss of soil as a result of unwise farming practices and by salinization and waterlogging of irrigated land. It is a victim because of the use for irrigation of polluted surface and groundwater, which in turn contaminate crops and transmit diseases to consumers and agricultural workers. Agriculture takes place in a symbiosis of land and water, as is clearly stated in the document FAO (1990a), "... appropriate measures be taken to prevent agricultural activities deteriorate the water quality and prevent future use of it for other purposes".

Since the seventies Europe has experienced a growing concern over the increase in waste nitrogen, phosphorous and pesticides into surface waters and groundwaters. The crop intensification has led to the conclusion already reached in France in 1980, that agriculture is an important factor non-point sources of contamination in surface water and groundwater (Ignazi, 1993).

Agriculture is also considered as the leading cause of groundwater pollution in the United States. In 1992, 49 of 50 states recognized in the nitrate, the major contaminant of groundwater, followed closely by pesticides. US-EPA (1994) concluded that "over 75 percent of the states recognized that agricultural activities represent a significant threat for the quality of groundwater."

It is difficult to obtain similar information in other countries and even in many cases are not collected or reported in a systematic way, in any case, numerous reports and studies indicate many developed and developing countries which have expressed similar concerns.

One of the most important factors in agricultural pollution, is the often limited relevance about the magnitude of the problem, given by public and private sectors directly involved in water management and in the development of prevention programs.

High concentrations of nitrates and pesticides in groundwater and surface water affect many urban areas, which use them as a source of potable water for domestic consumption. In addition to potential effects on the population, constitute a serious threat to water quality by cumulative.

El Valle del Carrizo, Sinaloa, Mexico is mainly devoted to agriculture, which represents the most important resources for the inhabitants. The agriculture production deeply influences population growth and the change in the socio economic development of this environment.The same applies to the north of Sinaloa and in general in the state's agricultural sectors.

The decisions to be taken in the agriculture sector against environmental pollution can be at different levels. In the field, decisions depend on very local factors such as type of crops and techniques of land use, including the use of fertilizers and pesticides. These decisions should be guided by best practice management to allow local circumstances, and the aim should be to multiply the profitability of farmers without forgetting the protection of the environment. Local decisions are based on known relationships between agricultural practices and environmental degradation, but usually do not require a specific assessment of agricultural practices in the broader context of the effects on watersheds caused by other types of pollution.

This paper offers specific recommendations. However, the problem facing sustainable agriculture is to improve environmental protection awareness and make it available to farmers.

Problem description

With regard to environmental pollution, deteriorating water quality is one of the biggest problems associated with pesticide use. This may be due to one of the following: dispersion, leaching and percolation into ground water (Boesten and Van der Pas, 2000), washing of equipment and application elements in water sources, improper disposal of waste pesticides and containers, broken containers and roll-over accident product into water sources (Boroukhovitch, 1992). The contamination of soil may be due to the direct application of pesticides (herbicides pre-emergence) to the ground to throughfall and stemflow from the plant, drifting of the spray and the improper disposal of residual spray or on packaging.

Overuse of chemicals used on crops is a major cause of pollution of water bodies (Richters, 1995; UNEP, 2001) constitutes an important environmental problem (Boesten and Van der Pas, 2000) that due to its persistence in soil can take years to degrade (Gonzalez and Illescas, 1987).

This involves negative effects on human health caused by accumulation of organic solids, toxic chemicals and heavy metals in soil, groundwater and surface water (UNEP, 2001).

The irrigation district 076, Valle del Carrizo is greatly impacted by problems of natural resources degradation, mainly concerning the use and management of water bodies. This has been expressed by residents of the place to prioritize this issue as one of the major environmental concerns, socially and economically to the general population.

The pollution of surface water Irrigation District 076, that threatens the natural ecosystem of the area (used as recreation areas) and impacts over the uses of water supplied from the reservoir throughout the valley (drinking water supply, agricultural irrigation and domestic purposes), creates adverse sanitary effects and contributes to the disappearance of native and migratory bird species with negative effects also against vegetation.

The intensive use of agrochemicals has led to the impoverishment of the soil and biodiversity, with adverse effects against groundwater and surface water (including coastal and marine waters) and negative sanitary effects against human receptors. A sound management of chemical pesticides should take advantage of the benefits arising from their use in destroying pests at the same time reducing risk to human health and environment.Actually measures do exist with the main purpose of reducing dependence from chemical pesticides, especially those too dangerous, maintaining at the same time viable production rates of agricultural crops.

On the other hand, point source pollution of agrochemicals generated at the facilities where containers are handled receive generally no attention, but, when such contaminant concentrations as large as those one detected in the Valle del Carrizo occur, no alternative choice is feasible to a proper and safe management of the process. Two are the main goals to be achieved at the same time: to maintain a decent quality of life in an reasonably preserved environment and avoid that the pollution mitigation and remediation measures adverse the economic activity that has generated the wastes.

Until today, because either lack of environmental awareness among farmers or feasible alternatives, solid containers have been indiscriminately dumped in holes, depressions and ditches or completely burned (getting an apparent elimination of the primary contamination source). A water quality worsening affect surface waters so it is essential to improve knowledge about the quality of surface waters in the Valle del Carrizo (Sinaloa) so to forecast the evolution of the contamination in order to guide actions and policies for future management of water, to lower risk pollution and to improve the sustainability of agriculture and water resources of Sinaloa state and Mexico.

The results of this research will help the authorities, responsible for water management and health and environment protection, to better control and prevent pollution in vulnerable areas and will serve as a tool to implement, along with producers, a strategy of sustainable development of the productive activities of Valle del Carrizo.

Main goal

The main goal of the research is to determine the level of pollution by fertilizers and pesticides in surface waters of the Irrigation District 076, Valle del Carrizo.

Specific objectives are:

1. Collect more accurate survey-based data, among producers, about application rates of fertilizers and pesticides at the Irrigation District;
2. Analyze collected surface-water samples to identify and quantify nitrogen-based fertilizers and pesticides concentration in the Valle del Carrizo;
3. Assess the degree of contamination of surface water caused by the use of chemicals in the Valle del Carrizo.

Methodology

Study area

The study area is the Irrigation District 076, Valle del Carrizo, located in the mexican northern state of Sinaloa. Politically, it includes part of the municipalities of Ahome and El Fuerte, and is geographically located at latitude 26 º 05 ‘ north and longitude 108 º 53 ‘ west.

The northern border is the state of Sonora, south to the Sierra Madre Occidental, and to the west the area is delimited by the Gulf of California.

The agricultural activity is dominated by fields of maize and horticultural crops where nitrogen fertilizer, as urea, are applied at a high rate together with pesticides. Figure 1 shows the map of the Irrigation District 076 (Valle del Carrizo) with the distribution of the investigated irrigation modules.

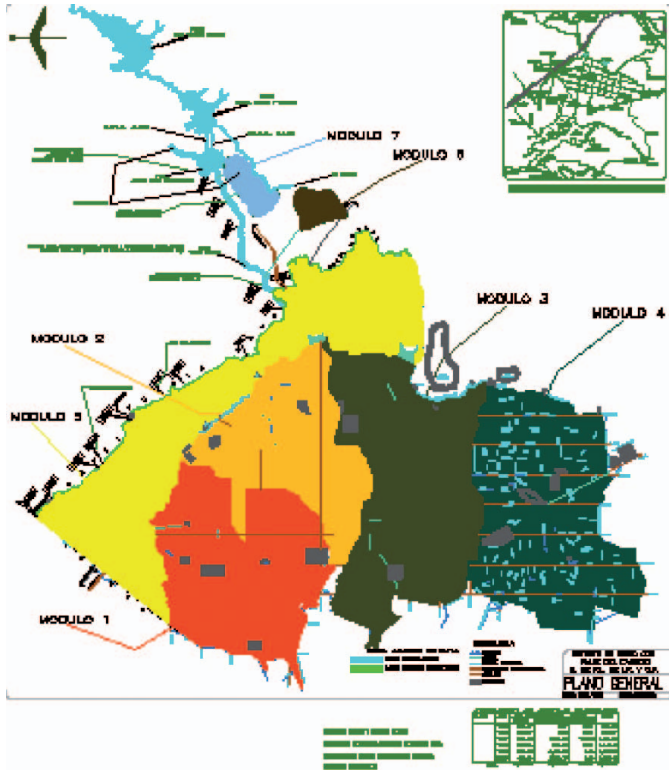

Fig. 1: *General Plan of Irrigation District 076, (Source: S.R.L.076, Valle del Carrizo)*

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Sampling of surface waters

For the monitoring of the surface waters of canals and ditches, the following criteria were chosen:

a) Sampling protocol of the British Geological Survey (BGS) was followed, similar to that one adopted by US-EPA and Arizona Department of Enviromental Quality (USA);

b) Laboratory analyses of pesticides and fertilizers were performed in the Laboratory of Special Examinations of the Direction of Investigation and Postgraduation Studies of the Technological Institute of Sonora State;

Gas chromatography was used for the analysis of pesticides; for the analysis of fertilizers the method NMX-AA-026-SCFI-2001, for N-total, and NMX-AA-029-SCFI-2001, for P-total, were used; nitrate and nitrite ions were analyzed by the brucine method and reduction of cadmium.

Water samples were collected in 20 points of the District of Irrigation 076 Valley of the Reed-grass: 18 in 10 main ditch collectors along principal streets of the Valley, 2 at mouth to the sea. One is the mouth of the canal collector from Barobampo to Jitzamuri Bay and the other one of the canal Collector from Carrizo to Agiabampo Bay. At the mouth N-total, ammonia nitrogen ($N\text{-}NH_3$), organic nitrogen (N-Org), nitrates ($N\text{-}NO_3$) and nitrites ($N\text{-}NO_2$) were analyzed. Water samples, once delivered to the laboratory, were stored in freeze.

Points of sampling are coincident with the crossings of canals with the main streets of the District of Irrigation 076: street 800, street 400 and the International road Mexico 15. The two sampling points at the mouths of the canals are: one to the north of the District at the Agiabampo's Bay and the other in the southern part at the Jitzamuri's Bay (point of discharge of the Reed-grass and Barobampo canals respectively). The criterion of choice of sampling points was in order that the points of sampling could be easily accessible for future studies. Location of sampling points was georeferenced by GPS, defining UTM coordinates and permitting the visualization on a satellite image (Fig.2).

Fig. 2: *Satellite image of the Valley of the Reed-grass with the sampling points (source: Google Earth)*

Results

Fertilizers

The results of nitrates and nitrites analyses in the collector canals from El Carrizo Valley were compared with the maximum permissible limits (MPL) by NOM-127-SSA1-1994 (Table 1)

Table 1 provides the results of laboratory analyses for fertilizers (total nitrogen and total phosphorus, nitrite and nitrate residues with indication of standard exceeding. All nitrate values exceed the standard, 16 values exceed the nitrite standard.

Pesticides

It was not possible to detect residues of pesticides applied to corn as *methamidophos*, *dimethoate* and *glyphosate clorotalonyl* as the laboratory was not capable; by the way other persistent pesticides residues occurred such as *dieldrin*, *chlordane A*, *methoxychlor* and *malathion*. These compounds probably still appear to be sold on the black market, because their use is forbidden (Table 2).

Conclusions

The big load of fertilizers and pesticides applied in the district clearly reverberates in the quality of the residual irrigation water, putting a risk to the health of the exposed population, since the majority of the inhabitants of the Valley of the Reed-grass use canals irrigation water for domestic and recreative use and, in some cases, fro drinking.

Surface waters used in the District of Irrigation 076 (Valley of the Carrizo) are contaminated by fertilizers since they exceed to a great extent the NOM-001-ECOL-1996 maximum permissible limits (LMP) for total nitrogen (15 mg/L). On the other hand total phosphorus maximum permissible limits (LMP) of 5 mg/L it is never exceeded in any point. In some sampling point pesticide residues exceed permissible limits.

The results of this study about the analyses of water used for agricultural use address an important environmental issue. Very high concentration values for total nitrogen and for nitrite and nitrate, exceeding the NOM-001-ECOL-1996, are conveyed to the sea; moreover some pesticide, that were in use about 25 years ago for cotton cultivation, still persist (*dieldrin*, *clordano*, *metoxicloro* and *malatión*). It is so apparent the strong waters pollution by nitrogenous substances and pesticides in the surface waters of the Valley of the Reed-grass.

Taking into account the Valley of the Reed-grass as study area, it is observed that this one behaves as a fragile system, capable to attacks the ecosystem, as a consequence of the human action of the agricultural producers with the excessive use of agrochemical, expecially in relationship to nitrogen-based fertilizers.

The residents of the Valley of the Reed-grass (centers of citizens activity, schools with children and teenagers, government and not governmental organizations), they all are surrounded with cultivations. The only norms that must be fulfilled are the application of pesticides respecting either minimal periods of new applications to treated areas or distance of application from urbanized zones.

Norm applications should incorporate the knowledge and experience in agroecological pest control, taking also into account rural producers organizations (companies that offer non-chemical alternatives), agro-ecological controls and organic agriculture.

The results of this study will serve as a data-set useful to predict future scenarios, as well as to formulate strategies for environmental protection.

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Tab. 1: *Laboratory results of nitrogenous waste water (Source: Prepared by the results of the Center for Natural Resource Services. Instituto Tecnologico de Sonora. (2008)).*

SAMPLE	mg / L					
	N-Total	**P-Total**	**Nitrate N-NO_3**	**Nitrite N-N-NO_2**	**Nitrate excess**	**Nitrite excess**
1	1, 69	0, 14	84,02	0,55	74,02	Doesn't exceed
2	1, 40	0, 16	78,9	11,15	68,9	10,5
3	3, 59	0, 18	38,31	11,92	28,31	10,92
4	1, 96	0, 24	152,8	5,43	142,8	4,43
5	0, 95	0, 22	95,97	0	85,97	Doesn't exceed
6	0, 79	0, 26	88,3	1,81	78,3	0,81
7	1, 23	0, 29	50,39	11,27	40,39	10,27
8	1, 18	0, 14	104,77	3,11	94,77	2,11
9	2, 47	0, 11	114,92	7,99	104,92	6,99
10	2, 86	0, 03	128,68	0	118,68	Doesn't exceed
11	1, 80	0, 08	60,6	5,78	50,6	4,78
12	2, 52	0, 14	98,61	9,41	78,61	8,41
13	1, 85	0, 21	104,42	6,97	94,42	5,97
14	0, 84	0, 17	102,13	3,5	92,13	2,5
15	1, 23	0, 06	106,12	2,22	96,12	1,22
16	3, 7	0, 14	84,5	5,89	74,5	4,89
17	2, 64	0, 21	206,71	7,42	196,71	6,42
18	6, 27	0, 71	86,92	15,9	76,92	14,9
19	0, 51	0, 06	84,22	0,39	74,22	Doesn't exceed
20	3, 13	0, 10	158,77	9,66	148,77	8,66

Tab. 2: *Laboratory results of pesticide residues in water (Source: Prepared by the results of the Center for Natural Resource Services. Instituto Tecnologico de Sonora. (2008). N.D.: not detected. Some samples were not included in the table not showing any occurrence of pesticide residues*

	SAMPLE										
PESTICIDE	1	2	8	9	10	12	14	17	18	19	20
	(mg/L)										
Lindane	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.
Aldrin	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.
Dieldrin	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	4,15 X 10^{-5}	2,44 X 10^{-5}	N. D.
Endrin	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.
Chlordane A	N. D.	N. D.	N. D.	N. D.	N. D.	3,43 X 10^{-6}	3,61 X 10^{-6}	N. D.	N. D.	N. D.	N. D.
Heptachlor	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.
Heptachlor Expocide	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.
Methoxychlor	4,31 X 10^{-5}	1,07 X 10^{-5}	N. D.	N. D.	N. D.	N. D.	N. D.	1,35 X 10^{-5}	N. D.	N. D.	1,87 X 10^{-5}
Malathion	N. D.	N. D.	4,08 X 10^{-4}	4,62 X 10^{-4}	3,33 X 10^{-4}	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.
Paratión metílico	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.	N. D.

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