OPEN ACCESS
The Journal of Engineering and Exact Sciences – jCEC, Vol. 10 N. 10 (2024)
journal homepage: https://periodicos.ufv.br/jcec
eISSN: 2527-1075
ISSN: 2446-9416

Qualitative and quantitative analysis of pesticides identified in surface and groundwater in the western region of Algeria

Article Info:
Article history: Received 2024-10-11 / Accepted 2024-12-27 / Available online 2024-12-27
doi: 10.18540/jcecvl10iss10pp21120

Nadia Berkok
Laboratory of science, technology and process engineering (LSTGP), University of Sciences and Technology of Oran, Mohamed Boudiaf, BP 1505 El M'Naouer, 31000, Oran, Algeria.
E-mail: nadia.berkok@univ-usto.dz
Mohammed Hadjel
Laboratory of science, technology and process engineering (LSTGP), University of Sciences and Technology of Oran, Mohamed Boudiaf, BP 1505 El M'Naouer, 31000, Oran, Algeria.
E-mail: hadjel100@yahoo.fr
Omar Bentata
Laboratory of science, technology and process engineering (LSTGP), University of Sciences and Technology of Oran, Mohamed Boudiaf, BP 1505 El M'Naouer, 31000, Oran, Algeria.
E-mail: omar.bentata@univ-usto.dz

Abstract
In this study, we are looking into the number of pesticides in a river for the West Tafna Watershed. Since it may be very difficult to detect pesticides in water, a sampling attempt was made at a number of control locations around the research region during the course of a two-year observation. Efforts are being made to identify and quantify pesticides like organochlorine, nitrogen, and phosphorous. Several techniques for extraction, purification, detection, and quantification were used after sampling. Liquid extraction method was used to remove pesticides from water. The samples and various pesticide standards were previously selected in accordance with the results desired: Mix A is made up of sixteen pesticides, while Mix B and Mix 1 are each made up of seven pesticides that are used for external calibration. Results showed that the content of many pesticides, including methylparathion (89.01 µg/L), azinophosphate-methyl (56.66 µg/L), O-ethyl phenylthiophosphazene (195.98 µg/L), and O-4-nitro phenyl (NHB), is much higher than the current limitations of 1.0 µg/L for surface water. The same chemicals are present in groundwater at excessive numbers that include: EPN 209.54 µg/L, Azinophosphate-methyl 183.01 µg/L, 2,4,5-T methyl ester 149.13 µg/L, Dichlorvos 143.43 µg/L, Thiophosphate of O,O-dimethyl and O-2,4,5-trichlorophenol (Ronnel) 57.18 µg/L, Diazinon 55.37 µg/L and Parathion 52.61 µg/L.
Keywords: Pollution, Pesticide, Micropollutant, Tafna catchment.

Nomenclature

ANRH	National Agency for Hydraulic Resources
WHO	World Health Organization
CE	European committee standard

1. Introduction

The use of pesticides affects the soil, water, and air as well as the rest of the natural world (Tudi *et al*., 2021; Liu *et al*. 2021). All areas of the ecosystem might get contaminated by the usage of plant protection products. Pesticide breakdown and dispersion begin as soon as phytosanitary chemicals are applied to the soil (Navarro *et al*., 2013). The use of pesticides, which are frequently marketed as plant defense products and contain a wide range of chemicals to protect plants from harmful organisms and destroy other undesirables, is the main cause of contamination of water resources available in impoundments, Lakes and dams (Ho *et al*.,2019). Even if the amounts of pesticides lost by runoff appear little in comparison to the amounts used (Schriever *et al*.,2007), the widespread contamination of surface water by runoff continues to be a serious environmental issue since it lowers the quality of a natural resource. The catchment area appears to be the appropriate scale for the investigation of the effects of agricultural and phytosanitary activities on the quality of surface water (Molnar-Irimie *et al*., 2024; Carazo-Rojas *et al*., 2018). The industrial effluents and pollutants resulting from the intensive use of fertilizers, pesticides, sanitary products, agriculture and pharmaceuticals are the major causes of environmental pollution according to recent national studies (Appannagari, 2017). The methods allowing for the efficient use of pesticides were first created by Law dealing to phytosanitary protection (Kubiak-Hardiman *et al*., 2023). Several assessments conducted across the world have revealed that a considerable portion of the population is highly poisoned by pesticides or their residues, which are accumulated at progressively high quantities in fats as they go up the food chain (González-Rodríguez *et al*., 2011). Therefore, the industries should purify their effluents before releasing them into the natural environment in order to conform to ever-stricter laws (Rubirola, A., *et al*., 2019). For their part, scientists working in a variety of fields (chemistry, geology, agronomy, plant physiology, medicine, etc.) are becoming increasingly interested in finding and removing pollutants that are directly responsible for the emergence of ecosystem imbalances or severe, life-threatening disorders in both humans and animals (Derache, 1986). Unfortunately, the absence of water quality control measures and laboratories with expertise in the management of water pollution by micro-pollutants adds to the medium- and long-term decline of the living environment and of human health (Delemotte *et al*.,1987). In Algeria, several independent pesticide management organizations, were in charge of ensuring pesticide production (Omran *et al*., 2020). However, the import of pesticides and other related materials is now a specialization of many enterprises (Bertomeu-Sánchez., 2019). Accordingly, 400 phytosanitary products are approved in Algeria, and farmers mostly use about 40 of these substances. (Soudani *et al*.,2022). The National Agency for Hydraulic Resources (ANRH) has expressed interest in the watershed pollution assessment for the West of Algeria at several zones. Among of them, the Tefna basin, which has extensive pollution, making it one of the most current basins and a source of worry for those in charge of water management. Agricultural pesticides can have a biological influence on the entire ecosystem; especially water (Cooper, 1993). There are notable agricultural areas in this basin's upstream section. The groups of pesticides known as organochlorine and organophosphate have received little of our attention. The assessment is predicated on the parametric variable ranges that describe the natural water characteristics and are satisfied at stations unaffected by the network under investigation. To achieve this study, a sample effort was initiated at control locations throughout a two-year observation period.

2. Degradation and dispersion of pesticides

Pesticides, also known as plant protection products, agro-pharmaceuticals, and pest control agents, are substances applied to crops to ensure consistent agricultural production. Since the 1950s, there has been a significant evolution in the composition and application of these substances, which have been used since the earliest days of agriculture. These chemicals exert an exogenous influence on plant growth, enabling higher crop yields. Pesticides are typically categorized into three primary types based on the pests they target: herbicides, insecticides, and fungicides, which combat fungi, bacteria, and viruses (Srivastava *et al*., 2019). The environmental behavior of pesticides is characterized by several key phenomena, including volatilization losses during physical transport, losses due to chemical processes such as photolysis, hydrolysis, oxidation, and reactions with mineral surfaces, as well as bioaccumulation, transformation, and mineralization in soils and sediments facilitated by microbial activity. Additionally, pesticides can adsorb to solid particles, influencing their mobility and persistence in the environment. (As shown by Figure 1).

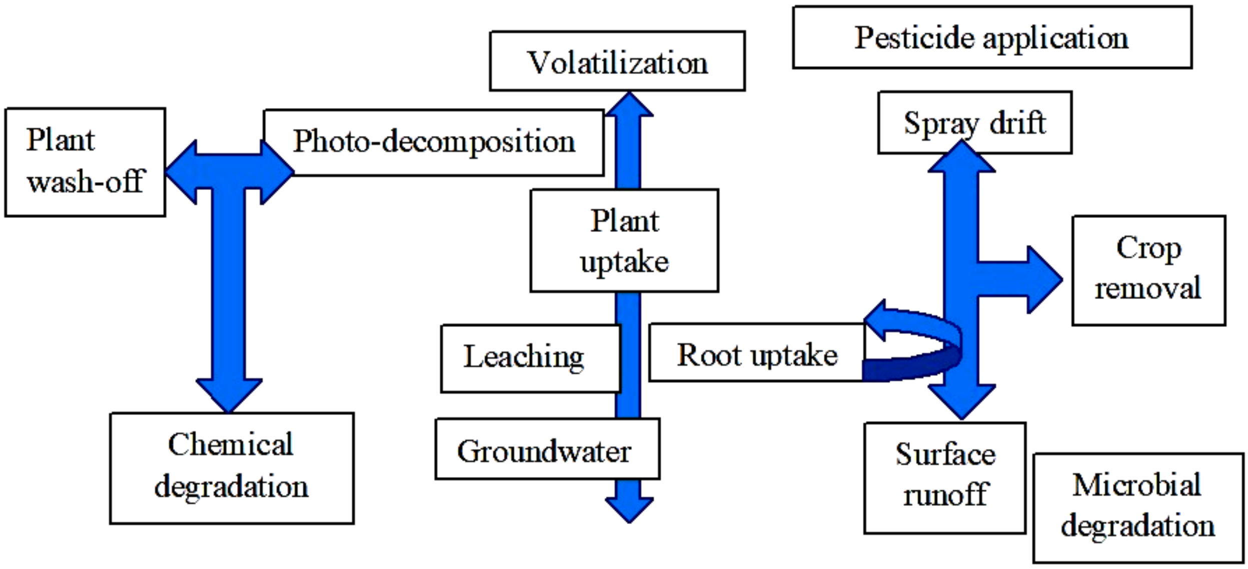

Figure 1 - Behavior of pesticides in the environment

3. Materials and methods

3.1 Area of investigation

The Tafna River's watershed is known for its dry semi-arid climate. During the year the average temperature is about 15.5°C; the two hottest months, July and August, have an average temperature of 26°C (Baba Hamed, 2001). (Tidjani *et al*., 2006; Zettam and all.,2017). The Tafna basin is mainly composed of Mediterranean forests and agriculture, horticulture which represent 70% of the total agricultural area. The main crop is wheat. with a population of 1.5 million (Zettam *et al*. 2020). The Tafna catchment region is separated into two geological zones: upstream, where the river runs in a canyon through Jurassic rocks rich in limestone and dolomite, and downstream, where the river runs in a tertiary basin characterized by marls covered with alluvial deposits reference.

Acquiring precise data is challenging since a product's sale in one area may not be indicative of its use in another. The pesticides used were identified and measured by a survey of farmers in the research region. Data on pesticide usage were derived from the regional directorate of Oran's survey. Due to the use of fertilizers, the treatment of the soil and plants, and the exploitation of the groundwater, the irrigated periphery of Maghnia, in particular the regions exploited in the Maghnia plain, is a potential source of pollution.

Water samples were gathered from multiple sites in the region (SP46, SP50, SP52, P1, P2) in order to categorize and measure the levels of pesticide, particular cation, and anion contamination. On-site, the pH of the solution is measured. The samples were transported in coolers to Oran, where they remained over the next few days undergoing testing at a National Agency for Hydraulic Resources (ANRH) analytical laboratory. The physico-chemistry of materials, catalysis, and environment laboratory extracted and concentrated their duplicates, and the samples are kept at -4°C. (As shown by Figure 2).

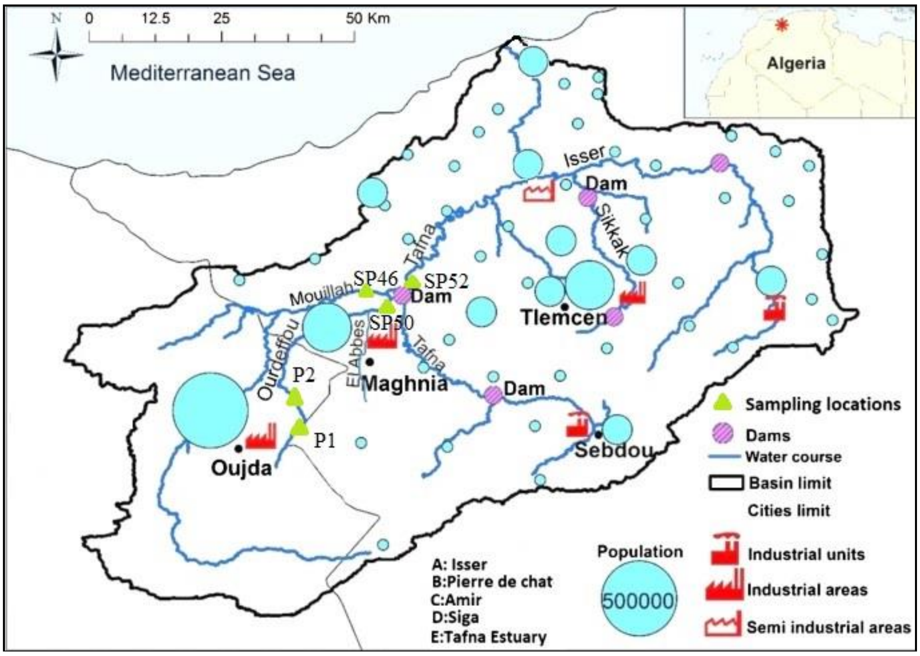

Figure 2 – The map of area of investigation

3.2 Sample Preparation

50 ml of solvent (petroleum ether or hexane) and 1 liter of water should be placed into a separating funnel before analysis. Manually mix 5 ml. In the container holding 10 g of sodium sulphate, decant the solution and recover the aqueous phase. Repeat the extraction once with 50 ml of solvent and once with 25 ml of solvent under the same conditions. In the same container, combine the organic phases and let them come into contact with the sodium sulfata for at least 30 minutes. Shake occasionally. Filter the organic phase through a small funnel containing a glass wool buffer that has been pre-washed with 50 cc of a solvent to get rid of the sodium sulphate crystals. Rinse the glass wool buffer with 10 cc of solvent after filtering (Colin, F. 2000). A rotary vacuum evaporator in a balloon heated to no more than 35°C in a water bath is not permitted to concentrate the organic solution from the extraction. After the volume reaches two milliliters, move it to a tiny graduated tube, rinse the flask with a small amount of solvent, and then attach it to the tube's contents. Using a stream of dry, pure air, evaporate the concentration at room temperature to reach 1 milliliter (Jean Rodier, 1996).

3.3 Equipment

Saturn 2200 GC/MS/MS (Schilling, K. E. 2009) was used. It consists of a Varian CP 3900 gas chromatograph with a universal 1079 capillary injector and coupled to a Saturn 2200 mass spectrometer. The data system contains all the software required for calibration, the GC/MS spectra collection and the computer for qualitative and quantitative analysis. In addition, it contains a NIST library with over one hundred and fifty thousand mass spectra for standard compounds. Separations were made by a 30 m capillary VF5 MS column of fused silica by Db-5.625 (Varian, Greek Watnut, CA, USA) coated with a thickness of 0.25µm phase. This phase is composed of 5% phenyl, polysiloxane and 95% methyl. The injector temperature was set to 255°C and 1µL was injected into the spit-mode. Samples were analyzed using a well-defined temperature program.

5. Results and discussion

5.1. Sampling

The agricultural character of the region surrounding the watercourses and surveys on pesticide use in the region were taken into consideration while choosing the measurement locations. The samples taken at the four different representative stations chosen in the Tafna mean are represented by a station in the Boughrara Dam and another station upstream of Oued Mouillah (SP46 surface water). Two more groundwater stations were chosen: one in Brazi (P2 groundwater) and one in

Herichi (P1 groundwater). Keep in mind that samples from stations SP46 and SP52 are surface water, while samples P1 and P2 are groundwater. Mathematically, the concentrations of the different kinds of pesticides found for use in various applications were inferred from the surfaces of the peaks of the chromatograms of the standards and the scales.

Tables 1, 2,3 give the amounts of the different kinds of pesticides found for each sample we looked at were indirectly calculated mathematically using the surfaces of the peaks of the various chromatograms of the standards and the scales.

Table 1 – The different pesticides present in the Mix A standard

Pesticide standard in Mix A	Formula	Retention time (min)
Azinophos methyl	C10H12N3O3PS2	20,123
Bolstar	C12H19O2PS3	17,547
Chlorpyrifos	C9H11Cl3NO3PS	13,782
Coumaphos	C14H16clO5PS	21,538
Diazinon	C12H21N2O3PS	11,489
Dichlorvos	C4H7Cl2O4P	5,404
Disulfoton	C8H19O2PS3	11,809
Ethoprophos	C8H19O2PS2	9,657
Fention	C10H15O2PS2	13,93
Merphos	C12H27PS3	14,825
Methyl parathion	C8H10NO5PS	12,884
Mevinphos	C7H13O6P	7,152
Naled	C4H7Br2Cl2O4P	9,934
Ronnel	C8H8Cl3O3PS	13,103
Tokuthion	C11H15Cl2O2PS2	15,984
Trichloronate	C10H12Cl3O3PS	14,213

Table 2 – The different pesticides present in the Mix B standard

Pesticide standard in Mix B	Formula	Retention time (min)
Dimethoate	C5H12NO3PS2	10,841
EPN	C14H14NO4PS	19,139
Malathion	C10H19O6 PS2	13,549
Monocrotophos	C7H14NO5P	10,2
Parathion	C10H14NO5PS	13,938
Sulfotep	C8H20O5P2S2	9,995
Tetraethyl pyrophosphate	C8H20O7P2	9,995

Table 3 – The different pesticides present in the Mix 1 standard

Pesticide standard in Mix 1	Formula	Retention time (min)
2,4-D methyl ester	C9H8Cl2O3	9,64
2,4-DB methyl ester	C9H8Cl2O3	12,318
Dicamba methyl ester	C9H8Cl2O3	8,244
Dinoseb methyl ether	C11H14N2O5	12,26
2,4,5-T methyl ester	C9H7Cl3O3	11,474
2,4,5-TP methyl ester (Silvex)	C10H9Cl3O3	11,061
Dichlorprop methyl ether	C10H10Cl2O3	9,322

As shown by Figure 3, several pesticides were present; according to our analyses at the second control point SP52. Most of them are found in the first station SP46 as well, and all of them are out over CE standard of 1.0 g / l. (the European Committee). This monitoring station contained: EPN, Azinophosphate-methyl, Coumaphos, Diazinon, Mevinphos, and methyl parathion in concentrations of 238.49 g/L, 157.71 g/L, 136.3 g/L, 75.78 g/L, 58.67 g/L, and 40.23 g/L, respectively. Pesticides may also be readily absorbed through fissures and contaminate groundwater during rainy seasons due to the loamy soil and fissured structure of most of the sites examined in the middle Tafna watershed (Spliid and Koppen, 1998).

However, we discover that at the second station, the purity of methyl parathion has dropped from 89.01 g/L to 40.23 g/L. We think that the Tafna dam's mobilization of diluted surface water and Oued Mouillah's capacity for self-treatment are to blame for this. This explains the massive concentrations of pesticides that have already been discovered in the same study region's surface waters, which are significantly higher than the WHO and drinking water limit of 0.1 g/L for all pesticides: Along with azinophosphate-methyl, 2,4,5-T methyl ester, dichlorvos, ronnel, 57.18 g/L, diazinon, 55.37 g/L, and parathion, 52.61 g/L, EPN was found to be 209.54 g/L.

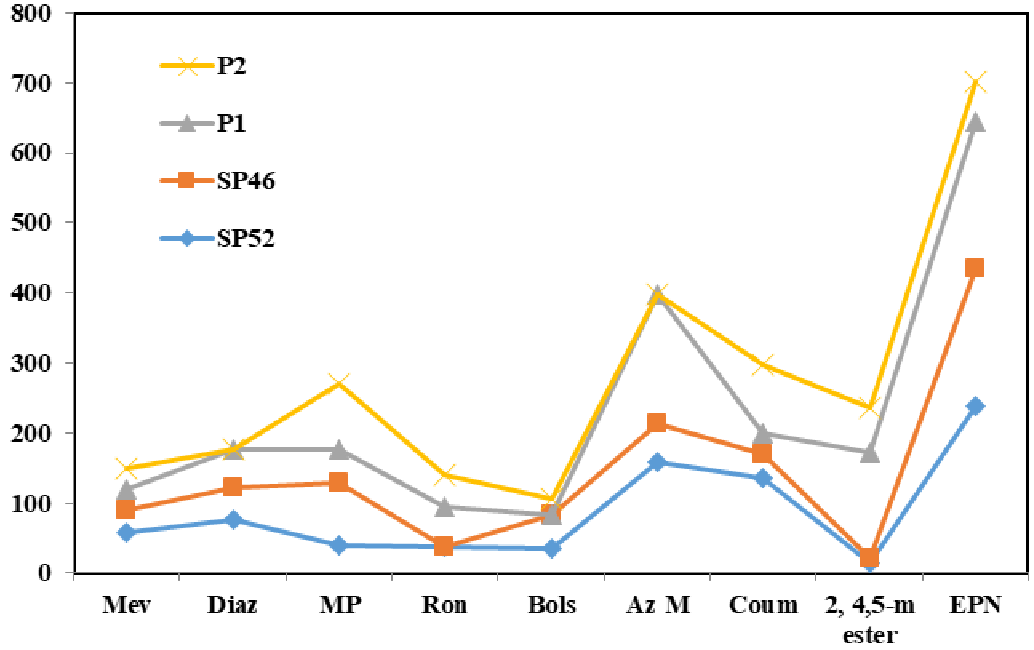

Figure 3 – Pesticides in groundwater and surface water

6. Conclusion

In summary, we were able to identify the use of phytosanitary products in the studied area thanks to our research. Three pesticide compounds-organochlorine, phosphorus, and nitrogen—have been identified as potentially present in surface and groundwater.Surface waters already include three of the eight pesticide chemicals we have identified in groundwater. Furthermore, it has been demonstrated that some pesticides have higher quantities in groundwater due to their penetration through the often permeable soils in the area.In order to raise user awareness of agricultural plant protection products, alert water management decision-makers to the threat of pollution, and ultimately enable the protection of wildlife, plants, and the environment, it would be desirable to integrate pesticide analysis into the monitoring and control of water quality..

These two insecticides are present and are lowering the quality of the surface waters in western Algeria, according to the results of numerous trips for the collection of water samples, extensive research in various labs involving extractions, the creation of standard solutions, qualitative and quantitative microanalyses using a variety of analytical techniques, particularly CPG and CG/MS, and the interpretation of the results from the obtained spectra. Overall, this analysis demonstrates that each of our groundwater tests had quite high pesticide levels.

Acknowledgements

The authors thank the Directorate General of Scientific Research and Technological Development (DGRSDT), and the Laboratory of Science, Technology and Process Engineering, U. S. T. Oran, Algeria.

References

Appannagari, R. R. (2017). Environmental pollution causes and consequences: a study. North Asian International Research Journal of Social Science & Humanities, 3(8), 151-161.

BABA-HAMED, K. (2001). Contribution à l'étude hydrologique de trois sous-bassins de la Tafna (bassin de Sebdou, de Mouilah et d'Isser). Mémoire de Magistère, Univ. Oran, Algérie, 195p. https://doi.org/10.1111/j.1365-3091.1977.tb00131.x

Bertomeu-Sánchez, J. R. (2019). Introduction. Pesticides: past and present. HoST-Journal of History of Science and Technology, 13(1), 1-27. https://10.2478/host-2019-0001

Carazo-Rojas, E., Pérez-Rojas, G., Pérez-Villanueva, M., Chinchilla-Soto, C., Chin-Pampillo, J. S., Aguilar-Mora, P., & Vryzas, Z. (2018). Pesticide monitoring and ecotoxicological risk assessment in surface water bodies and sediments of a tropical agro-ecosystem. Environmental Pollution, 241, 800-809. https://doi.org/10.1016/j.envpol.2018.06.020

Colin, F. (2000). Approche spatiale de la pollution chronique des eaux de surface par les produits phytosanitaires. Cas de l'atrazine dans le bassin versant du Sousson (Gers, France) (Doctoral dissertation, Doctorat Sciences de l'Eau, ENGREF Montpellier). https://hal.inrae.fr/tel-02580074

Cooper, C. M. (1993). Biological effects of agriculturally derived surface water pollutants on aquatic systems—a review. Journal of Environmental Quality, 22(3), 402-408. https://doi.org/10.2134/jeq1993.00472425002200030003x

Delmotte, M., & Jullien, H. (1987, July). Variations des caractéristiques diélectriques des résines époxydes au cours de leur réticulation sous microondes. Makromolekulare Chemie. Macromolecular Symposia, 9(1), 185-191. https://doi.org/10.1002/masy.19870090120

Derache, R. (1986). Toxicologie et sécurité des aliments. Paris, APRIA.

González-Rodríguez, R. M., Rial-Otero, R., Cancho-Grande, B., Gonzalez-Barreiro, C., & Simal-Gándara, J. (2011). A review on the fate of pesticides during the processes within the food-production chain. Critical Reviews in Food Science and Nutrition, 51(2), 99-114. https://doi.org/10.1080/10408390903432625

Handford, C. E., Elliott, C. T., & Campbell, K. (2015). A review of the global pesticide legislation and the scale of challenge in reaching the global harmonization of food safety standards. Integrated Environmental Assessment and Management, 11(4), 525-536. https://doi.org/10.1002/ieam.1635

Ho, L. T., & Goethals, P. L. M. (2019). Opportunities and challenges for the sustainability of lakes and reservoirs in relation to the Sustainable Development Goals (SDGs). Water, 11(7), 1462. https://doi.org/10.3390/w11071462

Jean Rodier. (1996). Analyse de l'eau. Édition Dunod.

Kubiak-Hardiman, P., Haughey, S. A., Meneely, J., Miller, S., Banerjee, K., & Elliott, C. T. (2023). Identifying gaps and challenges in global pesticide legislation that impact the protection of consumer health: Rice as a case study. Exposure and Health, 15(3), 597-618. https://doi.org/10.1007/s12403-022-00508-x

Liu, J., Zhou, J. H., Guo, Q. N., Ma, L. Y., & Yang, H. (2021). Physiochemical assessment of environmental behaviors of herbicide atrazine in soils associated with its degradation and bioavailability to weeds. Chemosphere, 262, 127830. https://doi.org/10.1016/j.chemosphere.2020.127830

Molnar-Irimie, A., Ranta, O., Stanilă, S., Marian, O., & Gheţe, A. (2024). Research on Methods to Reduce Water Pollution Due to Phytosanitary Treatments. Bulletin of the University of Agricultural Sciences & Veterinary Medicine Cluj-Napoca. Agriculture, 81(2). https://10.15835/buasvmcn-agr:2024.0008

Navarro, S., Vela, N., & Navarro, G. (2013). Review. An overview on the environmental behaviour of pesticide residues in soils. Spanish Journal of Agricultural Research, 5(3), 357-375. https://doi.org/10.5424/sjar/2007053-5344

Omran, E. S. E., & Negm, A. (2020). Impacts of pesticides on soil and water resources in Algeria. Water Resources in Algeria-Part I: Assessment of Surface and Groundwater Resources, 69-91. https://doi.org/10.1007/698_2020_468

Rubirola, A., Boleda, M. R., Galceran, M. T., & Moyano, E. (2019). Formation of new disinfection by-products of priority substances (Directive 2013/39/UE and Watch List) in drinking water treatment. Environmental Science and Pollution Research, 26(27), 28270-28283. https://doi.org/10.1007/s11356-019-06018-9

Schilling, K. E. (2009). Investigating local variation in groundwater recharge along a topographic gradient, Walnut Creek, Iowa, USA. Hydrogeology Journal, 17(2), 397. https://doi.org/10.1007/s10040-008-0347-5

Schriever, C. A., von der Ohe, P. C., & Liess, M. (2007). Estimating pesticide runoff in small streams. Chemosphere, 68(11), 2161-2171. https://doi.org/10.1016/j.chemosphere.2007.01.086

Soudani, N., Toumi, K., & Boukhalfa, H. H. (2022). Estimation of phytosanitary pressure and the environmental impact related to the use of pesticides. Egyptian Journal of Agricultural Research, 100(2), 184-192. https://10.21608/ejar.2022.98149.1157

Srivastava, A. K., & Kesavachandran, C. (2019). Health effects of pesticides. CRC Press.

Tidjani, A. E. B., Yebdri, D., Roth, J. C., & Derriche, Z. (2006). Exploration des séries chronologiques d'analyse de la qualité des eaux de surface dans le bassin de la Tafna (Algérie). Revue des Sciences de l'Eau, 19(4), 315-324. https://doi.org/10.7202/014418ar

Tudi, M., Daniel Ruan, H., Wang, L., Lyu, J., Sadler, R., Connell, D., Chu, C., & Phung, D. T. (2021). Agriculture Development, Pesticide Application and Its Impact on the Environment. International Journal of Environmental Research and Public Health, 18(3), 1112. https://doi.org/10.3390/ijerph18031112

Zettam, A., Taleb, A., Sauvage, S., Boithias, L., Belaidi, N., & Sánchez-Pérez, J. M. (2017). Modelling hydrology and sediment transport in a semi-arid and anthropized catchment using the SWAT model: The case of the Tafna river (northwest Algeria). Water, 9(3), 216. https://doi.org/10.3390/w9030216

Zettam, A., Taleb, A., Sauvage, S., Boithias, L., Belaidi, N., & Sánchez-Pérez, J. M. (2020). Applications of a SWAT model to evaluate the contribution of the Tafna catchment (north-west Africa) to the nitrate load entering the Mediterranean Sea. Environmental Monitoring and Assessment, 192, 1-17. https://doi.org/10.1007/s10661-020-08482-0