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FOOTPRINT AND DIRECT IMPACT OF ANTHROPOGENIC ACTIVITIES ON GROUNDWATERS FROM MEDIAS AREA

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ABSTRACT. Groundwater represents an important and direct source of fresh water, vulnerable to contamination. Groundwater composition is easily influenced by anthropogenic activities. Lack of sewerage facilities impress direct footprint on groundwater composition. Nitrogen compounds (NO_2^-, NO_3^-, NH_4^+), SO_4^{2-}, K^+, Cl^-, Mg^{2+}, Ca^{2+}, Na^+, pH and total dissolved solids were analysed from seven well waters from Medias area. The results showed the seasonal variation of analysed parameters, the nitrogen compounds, K^+ and Ca^{2+} exceeding the maximum admissible concentration in the majority of samples. The Stiff and Piper diagrams confirmed that the studied waters are Ca-HCO_3 type and have the same sources.

Keywords: *groundwater, anthropogenic activity, chemical composition, Piper diagram, Stiff diagram*

INTRODUCTION

Groundwater constitutes the largest fresh water reservoir (97%), while surface waters represent the other 3% of the freshwater sources [1].

Groundwater is a natural and free resource directly used by the inhabitants from areas where water from wells is used as freshwater source. Worldwide, natural and anthropogenic activities may influence the groundwater composition, altering its quality [2-4]. Pressure on groundwater quality and quantity exists also in the EU. Footprint and direct impact of anthropogenic activities on the groundwater quality were determined all over the world [5-7]. Abundant use of pesticides, nitrogen fertilizers, land drainage and land sealing, population density, water abstraction for industrial purposes and for public supply are human interventions with negative effects on groundwater composition and quality [8-11]. In Romania, the main problems are related to contamination of groundwater, with nitrogen

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compounds and organic substances both in rural and urban areas, due to the lack of sewerage facilities and poor agricultural practices [12]. Nitrogen compounds have two main sources: agricultural and non-agricultural. The population density is a variable non-agricultural source of nitrogen compounds in urban areas. Nitrogen compounds loadings are determined by septic systems, animal manure and fertilizers [13-14]. In the Romanian legislation, the threshold values for groundwater are specific for each groundwater body, considering their geological origin [15]. The footprint determination is significant for the establishment of the regional variations.

The aim of this study was to assess the groundwater footprint and direct impact of anthropogenic activities on groundwater as drinking water source (water wells) from Medias area, using samples collected from wells.

RESULTS AND DISCUSSION

The results show significant concentrations of chemical compounds in the studied well waters. High concentrations of nitrogen compounds (NO_2^-, NO_3^-, NH_4^+) and ions (SO_4^{2-}, Cl^-, K^+, Mg^{2+}, Ca^{2+}, Na^+) and high values of pH and total dissolved solids (TDS) were measured in all samples. Nitrogen compounds, calcium and sulphate concentration exceed the maximum admissible concentrations (MACs) established by the Romanian legislation [16], regarding quality of drinking water (Table 1). Furthermore, potassium concentrations exceed MAC established by World Health Organization [17]. High K^+ and Ca^{2+} concentrations are part of the natural geological matrix.

Table 1. Average composition of the studied waters and maximum admissible concentrations, for drinking and groundwater

Well	pH	TDS	NO_2^-	NO_3^-	NH_4^+	SO_4^{2-}	Cl^-	Mg^{2+}	K^+	Ca^{2+}	Na^+	HCO_3^-
		mg/l										
F1	8.5	438	**3.2**	39	**1.4**	145	80	27	**26**	194	136	281
F2	8.4	724	**2.4**	**101**	**0.5**	234	114	34	**33**	**212**	82	405
F3	8.3	719	**3.4**	**135**	**0.7**	**289**	104	28	**36**	**284**	83	483
F4	8.2	694	**<0.05**	**260**	**0.6**	239	45	23	**34**	**308**	87	519
F5	7.8	478	**5.1**	**229**	**3.0**	58	107	18	13	**260**	52	249
F6	8.4	551	**1.8**	**160**	0.4	197	87	15	13	**346**	55	433
F7	8.2	655	**3.3**	**202**	**0.7**	**277**	125	19	**100**	**448**	124	571
Maximum Admissible Concentration for drinking water*												
	8.5-9.5	-	0.5	50	0.5	250	250	-	-	200	200	-
Guideline values for drinking water**												
	-	-	3.0	50	-	-	-	200	20	-	-	-
Thresholds for groundwater***												
	-	-	0.5	-	0.8	250	250	-	-	-	-	-

* according to Law 311/2004 [16], ** according to WHO [17], *** according to Ministerial Order 621/2014 [15]

TDS varies during the year (November 2012 – May 2013). In the cold season (December 2012, January and February 2013), TDS levels were constant and high for samples F5 and F7 (415mg/l – 766mg/l), while in the rainy season (November 2012, March, April and May 2013) presents higher concentrations for the same samples (155mg/l – 865mg/l). Similarly, the chloride concentrations were the highest in the rainy season. The sample with the highest chloride concentration is F7 (43mg/l – 125mg/l) while sample F1 (9.3mg/l – 29mg/l) has the lowest values.

The Piper diagram (Figure 1) shows the dispersion of major cations and anions and classified the waters as Ca-HCO_3 type. All water samples are Ca-HCO_3 type. Stiff diagram represents the abundance of ions concentrations and variations between the water wells (Figure 2) and confirmed the fact that the major ions in the studied waters are Ca^{2+} and HCO_3^-.

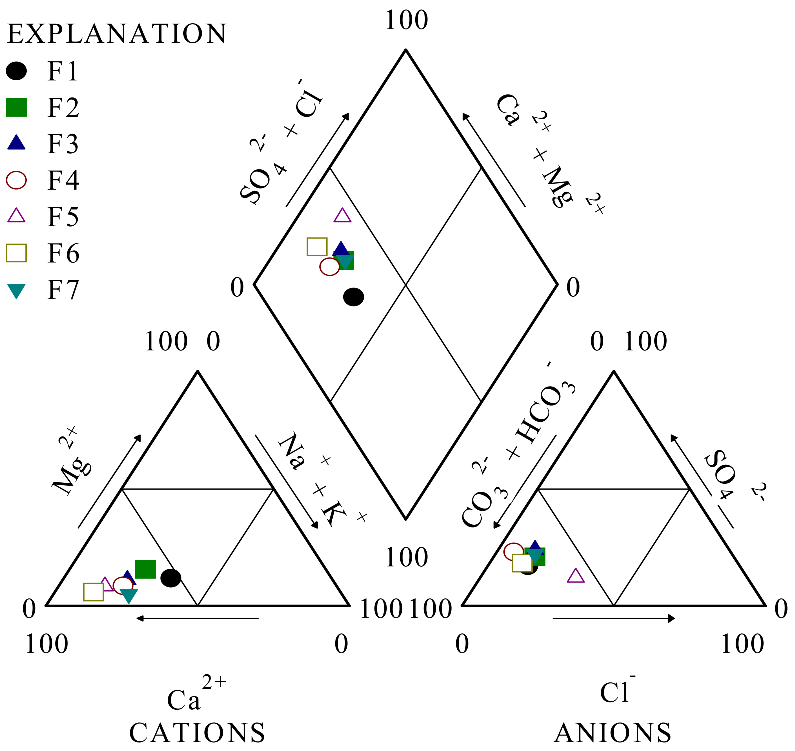

Figure 1. Representation of water types using Piper diagram

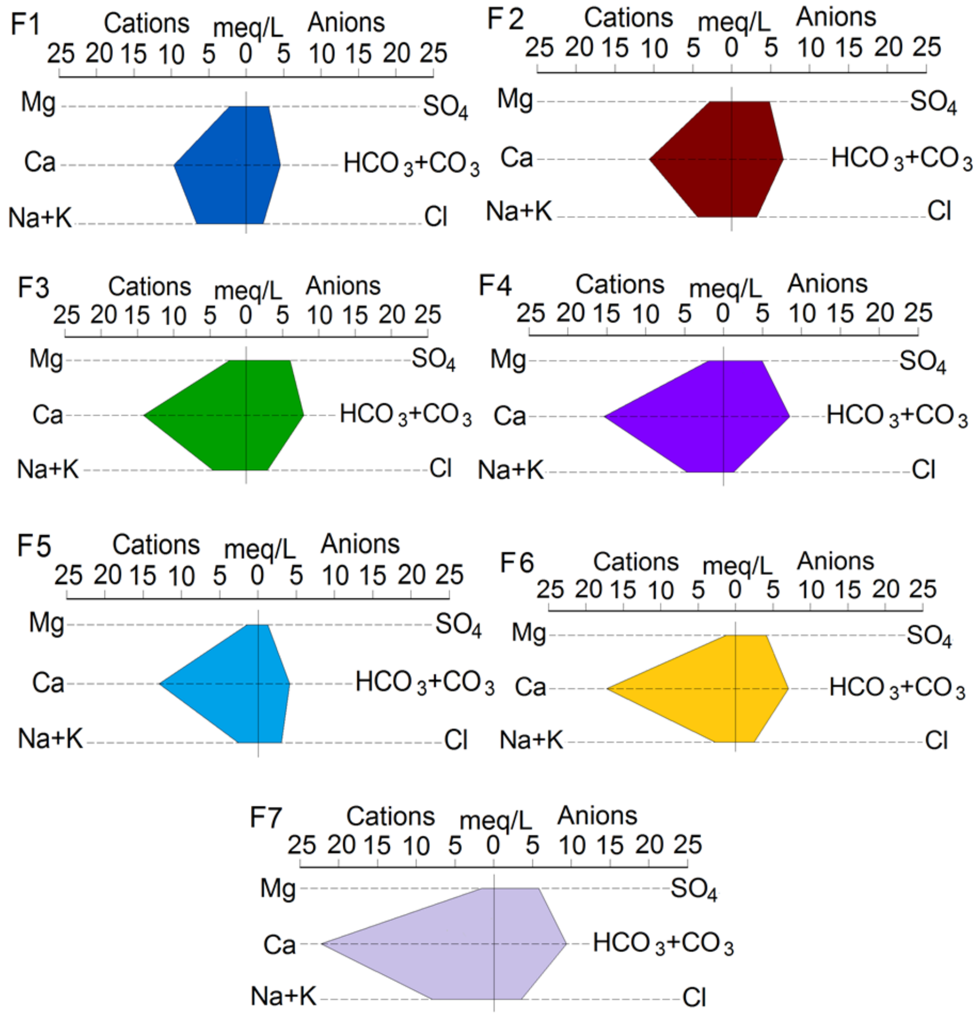

Figure 2. Stiff diagrams of average ions concentrations in wells waters (F1-F7)

Results show high concentrations for NO_2^-, NO_3^- and NH_4^+. In all samples except F1, the nitrate contents exceeded the MAC (50mg/l). The NO_3^- concentrations fluctuated during the year showing higher concentrations in the dry months than in the wetter period (Figure 3). The NO_2^- concentrations exceed six times the MAC (0.5mg/l) especially in the rainy period, as shown in Figure 4.

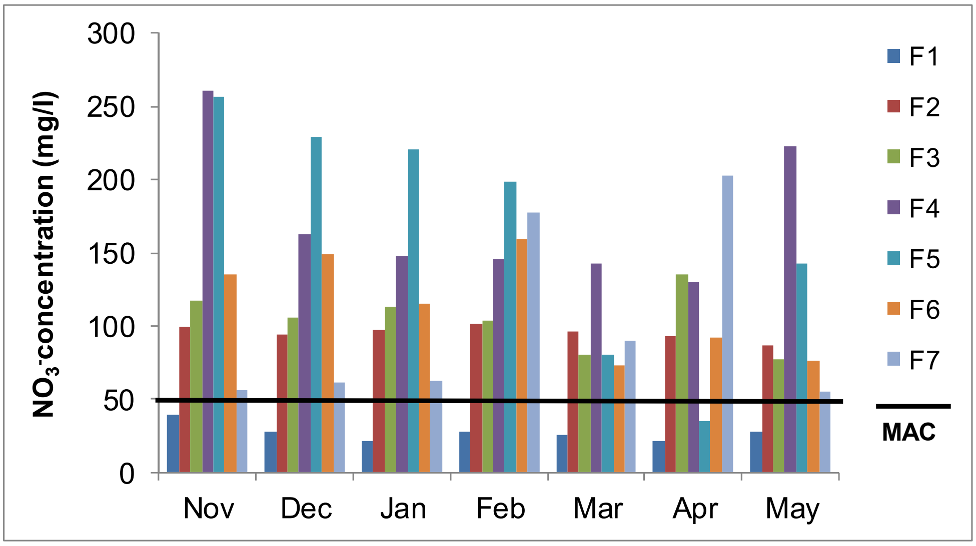

Figure 3. Monthly variation of NO_3^- concentration

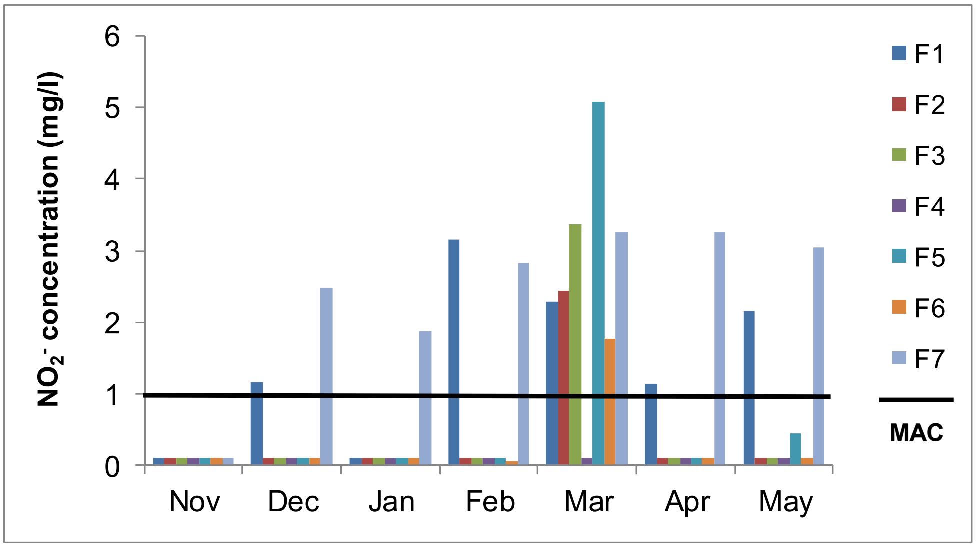

Figure 4. Monthly variation of NO_2^- concentration

Highest NO_3^- concentration is observed at sample F4 which is localized near (1m) to a former drain for household wastewater, manure water and rain water. Sample F4 has, also, 2 current toilets localized at 10m upstream. NO_2^- concentration exceeds MAC and reaches the highest concentration for sample F5 which has also the highest concentration for NH_4^+ exceeding MAC. The source of nitrogen compounds is an emptying pool situated at 3m distance, source that influence the pH of groundwater. Furthermore, F5 has the lowest value for pH. Sample F1 has the lowest NO_3^- concentration, but high concentrations for NO_2^- and NH_4^+. A current toilet is localized at 1.5m upstream from the water well, which means a permanent and continuous supply with nitrogen compounds.

The direct influence of the presented contamination sources can be demonstrated by the parameters variation with the distances between wells and pollution sources. Generally, samples localized very close to the sources have higher concentrations of NO_2^- and NO_3^- compared to those situated at longer distances (Figure 5).

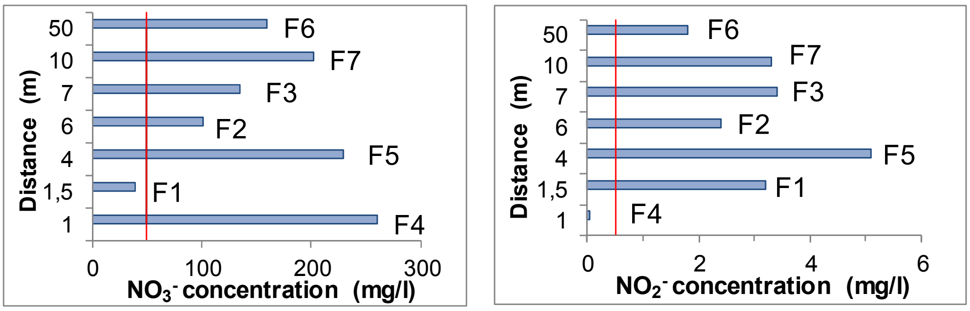

Figure 5. Relation of NO_3^- and NO_2^- concentrations in water with the distance between contamination source and well waters

All seven water wells are localized nearby anthropogenic sources, mostly sewerages. Thence, organic compounds are transferred from anthropogenic sources into the waters. It was observed a decrease of nitrogen compounds concentrations in rainy periods (stormwater dilutes the nitrogen compounds). The nitrogen compounds (NO_2^-, NO_3^- and NH_4^+) were identified in all samples, which imply the nitrogen transformations (nitrogen cycle: nitrification and denitrification).

CONCLUSIONS

Water wells from Medias area present high concentrations of nitrogen compounds (NO_2^-, NO_3^-, NH_4^+), that exceed the corresponding MACs [16-17]. Nitrogen compounds concentration varied during the sampling period (dry and rainy season). Sources for NO_2^-, NO_3^-, NH_4^+ are dry toilets, emptying pool, former stables, manure and straw stores localized at very short distances (5-10m) from water wells.

The SO_4^{2-}, K^+ and Ca^{2+} concentrations exceeded the MACs. Using Piper and Stiff diagrams, all water samples are Ca-HCO_3 type and have the same sources. The Na^+, K^+ and Ca^{2+} sources are the natural geological matrix.

EXPERIMENTAL SECTION

Description of the study area

Transylvanian town, Medias has about of 44.000 inhabitants and is localized in the central part of the Sibiu County. In Medias area, Miocene and Pliocene sediment deposits are the main geological formations. Sediment deposits are represented by sands that interlaid with grey marls, soft limestone and andesite tuffs. Medium hills (450-600m) with horizontal fragmentation less pronounced and smooth cliffs surround the city that is crossed from Vest to East by Tarnava Mare River. Annual temperature mean is 8 °C and the mean annual rainfall is higher than 600mm [18].

Water-bearing has a depth of 1.2-10m, with flow rates ranging from 0.2-8m/s. High hill areas are characterized with 5-10m depth aquifers and meadow hill areas with 5m depth aquifers. Between 250-300m bedding depth water bed has been found, but only in the sediment areas [19].

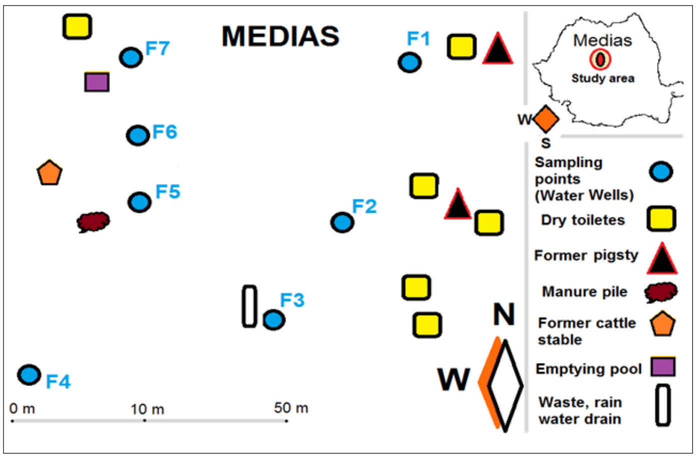

Figure 6. Sampling points and contamination sources

Seven private water wells from an old residential district inhabited by 13 % of the town's population, where the majority of the inhabitants lives in private houses and use well water as drinking water source were studied (Figure 6). Groundwater from Medias area is part of GWMU05 water body (Tarnava Mare river floodplain and terraces) with specific characteristics: industrial and agricultural pollution; groundwater is used in industrial, animal husbandry fields and for water supply [20].

Table 2. Characteristics for the studied water wells

Well	Distance from contamination sources (m)	Geographical coordinates	Age (years)	Depth (m)	Diameter (m)	Height above ground level (m)
F1	1.5m upstream from is a dry toilet and a former pigsty	46°8'56.34"N 24°22'10.64"E	25	5.0	1.25	0.00
F2	6m from an emptying pool	46°8'56.11"N 24°22'8.62"E	35	5.5	1.25	0.75
F3	6m downstream from a former cattle stable; 7m from a manure pile	46°8'55.35"N 24°22'8.32"E	38	5.0	1.25	1.00
F4	10m upstream from 2 dry toilets; 1m downstream from a former waste water drain	46°8'55.34"N 24°22'9.94"E	38	7.5	0.30	0.40
F5	4m from a dry toilet; 3m from an emptying pool	46°8'56.63"N 24°22'8.51"E	52	7.0	1.25	1.00
F6	50m downstream from a former cattle stable	46°8'54.34"N 24°22'8.28"E	48	4.5	0.40	0.00
F7	5 m upstream from a dry toilet; 10m upstream from a former pigsty and dry toilet	46°8'55.96"N 24°22'10.81"E	42	7.0	1.25	1.00

The studied water wells are at least 50 years old, with depths from 3 to 8m. People use the water from wells for house works, but also for drinking and cooking, although the wells location is nearby dry toilets, tank collectors, faces settlements and animal fenders (Table 2).

Sample collection

Since in the study area there are no other available access points to groundwater we chose as monitoring points the water wells used by locals as drinking water supply, as it reflects the footprint of the groundwater.

Samples were collected monthly between November 2012 and May 2013 (7 sampling campaigns) using hydrophore pump and bucket (for wells that had no hydrophore pump). Water samples were stored in 100ml polyethylene bottles (previously prewashed) and kept at 4 °C in a freezer. Before analysis samples were filtered using a plastic filter unit equipped with a 0.45μm cellulose acetate filter membrane.

Materials and methods

Instrumentation

A WTW *350 i* Multiparameter was used for the physicochemical parameters (pH and TDS).

Ions (Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, NH_4^+, Mg^{2+}, Ca^{2+}, Na^+, K^+) were analysed using ICS 1500 Dionex Ion Chromatography (IC) with suppressed conductivity detection. The instrument has two columns, one for anions determination and one for cations determination. The HCO_3^- content was determined by titration with HCl, against methyl orange indicator.

The abundance of ions in individual water samples, the nature of water wells and the relationships between water samples are presented with the help of two graphical approaches (Piper and Stiff diagrams) using the software GW Chart and AqQa 1.1.

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