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# ANTHROPOGENIC IMPACT OF URBAN SETTLEMENTS ON INORGANIC ANIONS CONTENT IN SELECTED WATERCOURSES IN THE SUBCARPATHIAN REGION OF POLAND

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## ABSTRACT

**Background.** Legislation for environmentally protecting surface waters in Poland and the EU is considered a priority because of the large human impact on this environmental feature in both highly industrialised countries as well as those that are agriculturally well developed. The biggest threats are regarded as being sewage arising from economic, industrial and agricultural pollution along with rain water run-off from fields treated with fertilizers. One of the most characteristic indicators of pollution exposure in surface waters are inorganic anions which form the principal components of town sewage and fertilizers.

**Objectives.** The estimate the effect that six selected sites of human settlement have on variously sized watercourses running through. The human environmental impact was based on determination of chlorides, nitrates and sulphates concentrations in such waters.

**Materials and Methods.** Water samples were obtained from the following rivers and towns, respectively; the Nil in Kolbuszowa, the Mleczka in Przeworsk, the San in Jaroslaw, the Wislok in Rzeszow, the Bystrzyca in Olimpow and an unnamed watercourse in Niwiska. Sampling sites were chosen at 4-6 points along each watercourse for a given locality. Analyte levels were measured by ion chromatography using the Dionex ICS 1000 instrument.

**Results.** Mean chlorides concentrations were found to vary from 8.52 (±0.17, n=3) mg/L to 78.41 (±0.19, n=3) mg/L, mean nitrates were 6.76 (±0.00, n=3) mg/L to 23.97 (±1.50, n=3) mg/L and mean sulphates from 29.89 (±1.57, n=3) mg/L to 62.48 (±2.99, n=3) mg/L. The clearest environmental effect of settlements on watercourses were observed for the small to medium sized towns of Kolbuszowa, Przeworsk and Jaroslaw in the form of frequently elevated chlorides levels from sewage.

**Conclusions.** By designating various sampling locations, along the watercourses for measuring the human environmental impact of nearby settlements, it is possible to identify sources of river pollution and thus take appropriate remedial action, as and when required.

**Key words:** *rivers, water pollution, chlorides, nitrates, sulphates, ion chromatography*

## STRESZCZENIE

**Wprowadzenie.** Ochrona wód powierzchniowych traktowana jest przez polskie i europejskie ustawodawstwo priorytetowo ze względu na wysoki stopień antropopresji na ten element środowiska, zarówno w krajach wysoko uprzemysłowionych jak i z rozwiniętą gospodarką rolną. Za najgroźniejsze uznaje się zanieczyszczenia ściekami bytowo-gospodarczymi, przemysłowymi i rolnymi, a także wodami opadowych z pól użyźnianych nawozami sztucznymi. Jednym z najbardziej charakterystycznych wskaźników narażenia wód powierzchniowych na zanieczyszczenia są aniony nieorganiczne, stanowiące składnik ścieków komunalnych i nawozów sztucznych.

**Cel badań.** Celem niniejszej pracy było oszacowanie wpływu wybranych sześciu jednostek osadniczych na przepływające przez nie różnej wielkości cieki wodne. Stopień antropopresji określony został na podstawie oznaczania zawartości chlorków, azotanów (V) i siarczanów (VI) na przebiegu cieku wodnego przez jednostkę osadniczą.

**Materiał i metody.** Próbki wody do badań pobierano z rzek: Nil w miejscowości Kolbuszowa, Mleczka w miejscowości Przeworsk, San w miejscowości Jarosław, Wisłok w miejscowości Rzeszów, Bystrzyca w miejscowości Olimpów i z bezimiennego cieku wodnego w miejscowości Niwiska. Miejsca pobierania próbek wytypowano w czterech do sześciu punktach cieku wodnego, charakterystycznych dla danej miejscowości. W pobranych próbkach oznaczano zawartość chlorków, azotanów (V) i siarczanów (VI) przy użyciu chromatografu jonowego Dionex ICS 1000.

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**Wyniki.** W badanych próbkach średnia zawartość chlorków wahała się od 8,52 (±0,17, n=3) mg/l do 78,41 (±0,19, n=3) mg/l, azotanów (V) od 6,76 (±0,00, n=3) mg/l do 23,97 (±1,50, n=3) mg/l i siarczanów (VI) od 29,89 (±1,57, n=3) mg/l do 62,48 (±2,99, n=3) mg/l. Najwyraźniejszy wpływ jednostek osadniczych na cieki wodne obserwowano w przypadku ich przebiegu przez małe i średnie miasta: Kolbuszową, Przeworsk i Jarosław. Antropopresja jednostek osadniczych manifestuje się najczęściej wzrostem stężeń chlorków będących składnikiem ścieków komunalnych.

**Wnioski.** Typowanie kilka punktów poboru próbek wody do badań, zlokalizowanych na odcinku cieku wodnego poddanego antropopresji, pozwala zidentyfikować źródła zanieczyszczeń rzek i ustanowić odpowiednie działania naprawcze.

**Słowa kluczowe:** *rzeki, zanieczyszczenia wody w rzekach, chlorki, azotany (V), siarczany (VI), chromatografia jonowa*

## INTRODUCTION

Sewage pollution is the most significant contaminant of Polish rivers which arises from urban areas, industry, rainwater run-off from fields as well as that from agriculture and farms [20]. Even though water quality has recently improved in Polish rivers, it still remains unsatisfactory, most usually due to the illegal discharging of waste water and direct discharges of contaminants. It is therefore important to not only achieve ecologically satisfactory levels, but to ensure they are always maintained and that self-purifying processes are monitored [2, 6, 19]. This can be achieved by keeping track of chosen analyte concentrations in river water with reference to the obligatory standards, in order that remedial action can be taken for ensuring improved surface water quality. One of the most often measured contaminants are inorganic anions like nitrates, nitrites, sulphates and chlorides [15, 18]. When these occur in high amounts they may cause harm to the aquatic environment [4, 14, 23].

Inorganic ions are most commonly measured by electrochemical or spectrophotometric methods which however do not always meet the modern day requirements of analytical instrumentation [12]. The adopted methods should also be highly sensitive, selective and ones that don't need large sample volumes. A method that fulfils these conditions is Ion Chromatography (IC), belonging to the HPLC range of methods (High Performance Liquid Chromatography) [7, 8, 9]. It is used for separating and detecting both organic and inorganic anions in samples of surface water, drinking water, rain water, other atmospheric precipitation, run-off water and waste water from industry and towns [3, 4, 10, 14], together with liquid foodstuffs and physiological liquids [1, 5, 7, 9].

The study aim was to determine inorganic anions in water samples taken from isolated points, selected along watercourses, with reference to the standard requirements set for surface water. In addition, it was possible to track changes in such analytes when flowing past sites of human settlement in order to assess their environmental impact.

## MATERIALS AND METHODS

Concentrations of chlorides, nitrates and sulphates were measured in water samples obtained from 6 rivers adjacent to towns in the Subcarpathian Province of Poland, respectively; the Nil in Kolbuszowa, the Mleczka in Przeworsk, the San in Jaroslaw, the Wislok in Rzeszow, the Bystrzyca in Olimpow and an unnamed watercourse in Niwiska; Figure 1, Table 1.

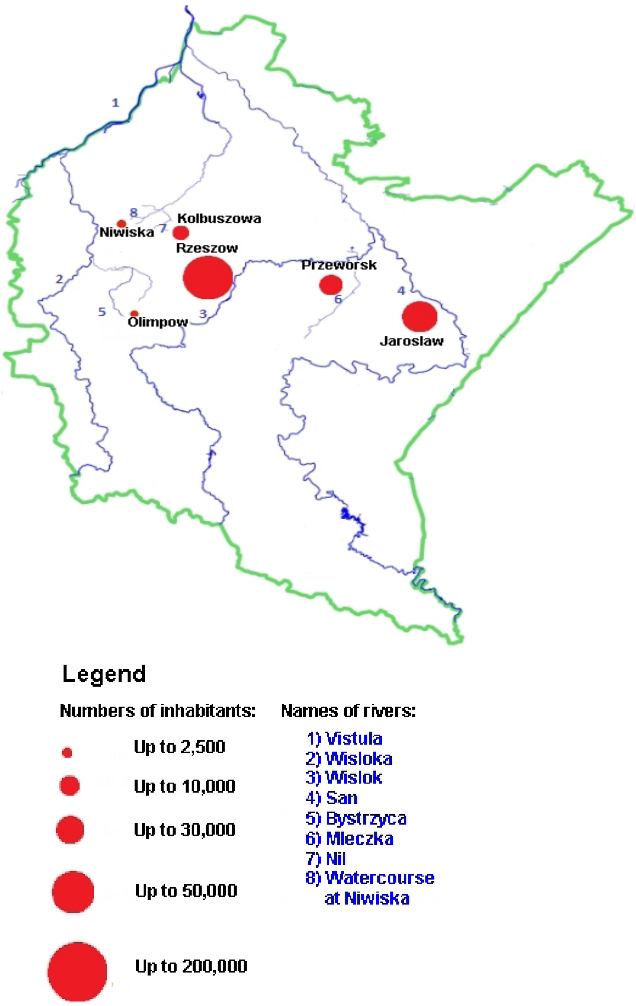


Figure 1. Map of the Subcarpathian Province in Poland showing sampling locations

Water samples were taken between 15th to 20th December 2013, after 2 weeks of high pressure weather,

Table 1. Study watercourses and settlements

| Watercourse | Watercourse length [km] | Town | Locations of sampling points [km along course] | Approximate number of inhabitants [thousands] |
|---|---|---|---|---|
| Bystrzyca | 25 | Olimpow | 3 – 7 | 0.6 |
| Mleczka | 37 | Przeworsk | 28 – 34 | 16 |
| Nil | 13 | Kolbuszowa | 3 – 7 | 9 |
| Watercourse in Niwiska | 4 | Niwiska | 1 – 2 | 1.6 |
| San | 443 | Jaroslaw | 160 – 178 | 39 |
| Wislok | 228 | Rzeszow | 144 – 165 | 185 |

no rain and a low water level. Sampling locations were next to human settlements at several specially selected sites. Discrete samples of water were placed into 50 mL, polyethylene 'Falcon' centrifuge tubes, previously rinsed with the test water. Actual samples were obtained from the watercourse surface layers by totally immersing, by hand, the sample containers about 1 meter away from riverbank and pointing towards the oncoming current. After sampling, the containers were so sealed as to avoid any air bubble [11] and then refrigerated and delivered for analyses to the Laboratory for Environment Health Analysis and Materials of Agricultural Origin at the University of Rzeszow's Department of Biology and Agriculture.

Samples were first degassed, prior to chromatography, by ultrasonication followed by passing through a 0.45 µm pore size MCE syringe filter. Chromatography was performed on the Dionex ICS 1000 instrument using run programming by the 'Chromeleon vers. 6.8' software. A standard solution of 7 anions was obtained from Thermo Scientific. The mobile phase was prepared by a 1:100 dilution of a stock solution 0.8 M $Na_2CO_3$ / 0.1 M $NaHCO_3$, whilst the analytical column was a dedicated Thermo Scientific 'Pack AS 14A' preceded by a AS 14G guard column; thermostatted at 30ºC. 25 µL of samples were run isocratically at a flow rate of 1 mL/min. Detection was by conductivity in a sample cell held at 35ºC. A ASRS-4 mm suppressor was used to suppress the conductivity of the mobile phase. Data read-out frequency was set at 5.0 Hz. Obtained chromatograms were constructed by the aforementioned Chromeleon programme.

Analyte concentrations of anions were calculated by a validated in-house procedure. Method specificity was confirmed by comparing test peak retention times with those of the standards. A linear analytical range over 1.0 to 50.0 mg/l was defined, where samples >50.0 mg/l were diluted and re-analysed. Method precision was obtained from triplicate runs of both standards and test samples. Concentrations were expressed as means, standard errors and numbers of replicates. Test concentrations were calculated from a previously run calibration, (yielding 5 point calibration curves), of a water sample containing the 7 standard inorganic anions.

## RESULTS

Mean chlorides concentrations in the test samples varied from 8.52 (±0.17, n=3) mg/l to 78.41 (±0.19, n=3) mg/L, mean nitrates were 6.76 (±0.00, n=3) mg/L to 23.97 (±1.50, n=3) mg/L and mean sulphates from 29.89 (±1.57, n=3) mg/L to 62.48 (±2.99, n=3) mg/L; Figure 2.

Water samples from the Bystrzyca river did not show any significant change in anion concentrations when passing by the Olimpow. Chlorides levels varied from 14.15 (±0.06, n=3) mg/L to 16.64 (±0.01, n=3) mg/L, nitrates from 7.63 (±0.08, n=3) mg/L to 8.79 (±0.09, n=3) mg/L and sulphates ranged from 49.73 (±0.15, n=3) mg/L to 60.33 (±0.03, n=3) mg/L; Figure 2.

Mleczka river samples showed a graded rise for all anion concentrations during its passage through the town of Przeworsk. For chlorides, levels at the first site were 17.49 (±1.00, n=3) mg/L that rose to 25.05 (±0.05, n=3) mg/L at the fifth point. Correspondingly, for nitrates this rose from 8.02 (±0.23, n=3) mg/L to 9.13 (±0.01, n=3) mg/L and likewise for sulphates from 29.89 (±1.57, n=3) mg/L to 39.20 (±011, n=3) mg/L; Figure 2.

Anions concentrations found in the Nil river held steady for the first 3 locations but all these rose at the 4th sampling point located after the inflow of the Kolbuszowka river that in its upper courses, passed through an area of intensive agricultural cultivation. At the 6th point, chlorides levels more than doubled; this being located after the mouth of a small inflowing watercourse that had previously passed by an industrial factory. When compared to the first location, the concentrations of anions at the 6th point increased as follows; chlorides from 11.7 (± 0.05, n = 3) mg/L to 78.41 (± 0.19, n = 3) mg/L, nitrates from 6.76 (± 0.00, n = 3) mg/L to 8.20 (± 0.04, n = 3) mg/L and sulphates from 29.56 (± 0.03, n = 3) mg/L to 48.37 (± 0.06, n = 3) mg/L; Figure 2.

There were no differences in anions content between the first 2 sampling points of the San river flowing through Jaroslaw town, however the third point located after a large industrial complex showed a threefold increase in chlorides compared to the previous sampling point i.e. 70.41 (±0.50, n=3) mg/L versus 19.24 (±0.08, n=3) mg/L. In subsequent points situated alongside resi-

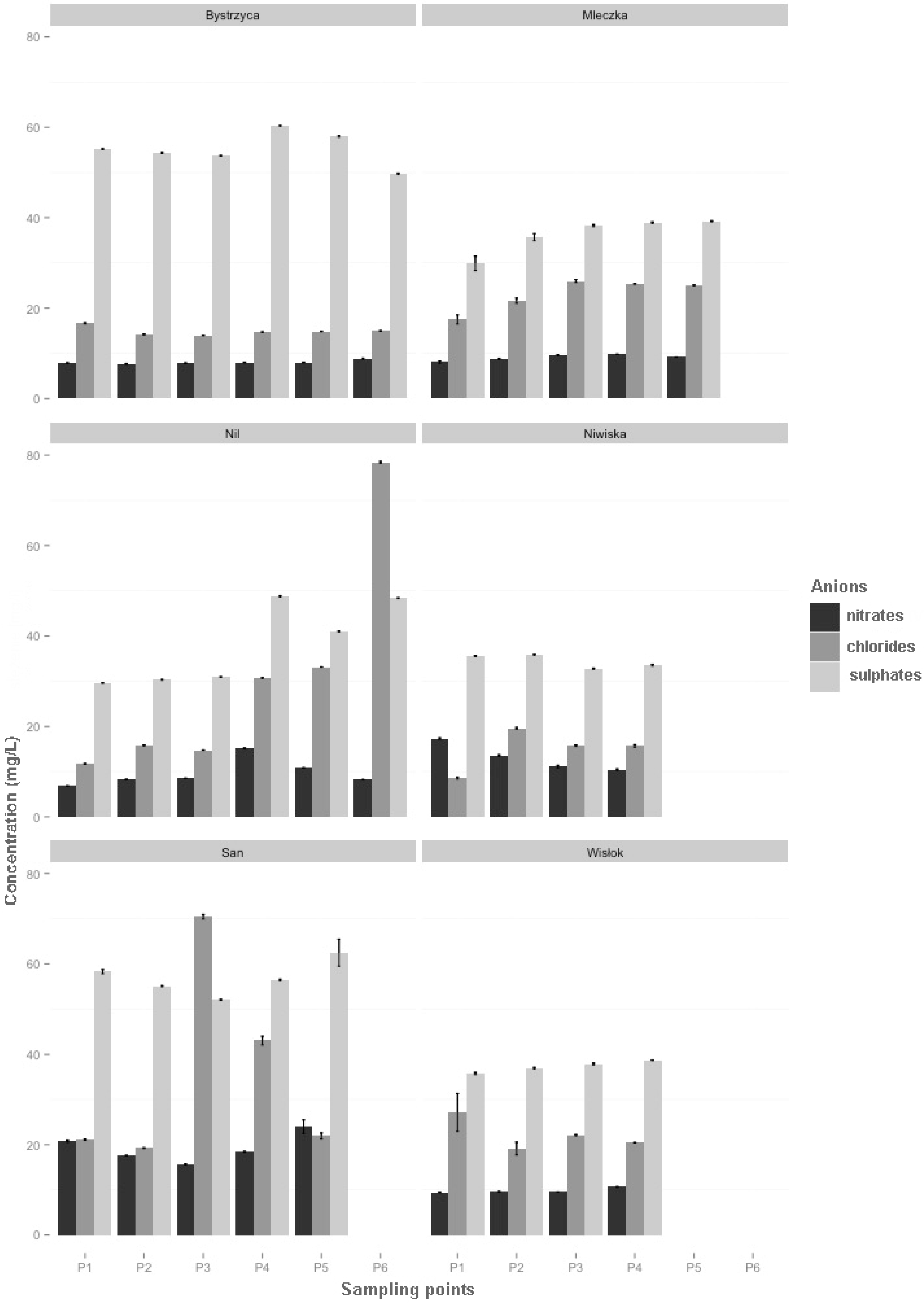


Figure 2 Mean concentrations of nitrates, chlorides and sulphates in successive sampling points along each studied watercourses

dential premises, chlorides concentrations fell to 21.90 (±0.67, n=3) mg/L at point five. Despite this, levels of nitrates rose from 15.64 (±0.05, n=3) mg/L at point 3 to 23.97 (±1.50, n=3) mg/L at point 5; likewise sulphates increased from 52.03 (±0.09, n=3) mg/L to 62.48 (±2.99, n=3) mg/L at the same points as previously mentioned.

For the inorganic anions measured in sampled waters of the Wislok river flowing through Rzeszow, there were no major differences observed at any of the points. At the first sample point, chlorides was 27.12 (±4.20, n=3) mg/L and 20.44 (±0.03, n=3) mg/L in the last. Correspondingly, the levels for nitrates were 9.43 (±0.01, n=3) mg/L versus 10.64 (±0.07, n=3) mg/L and 35.75 (±0.25, n=3) mg/L versus 38.69 (±0.06, n=3) mg/L for sulphates ; Figure 2.

## DISCUSSION

Markers of surface water quality have been described in the Polish scientific literature [13, 17, 18] and anions have been measured in watercourses at locations chosen by the regional Environmental Protection Inspectorate authorities, as part its monitoring system [20, 21]. Such studies however, most often deal with locations separated from each other.

Studies measuring chlorides, nitrates and sulphates in watercourses flowing through potential areas of contamination have however been undertaken by *Wójcik* and *Morawski* [23]. Five locations had been selected along the river Wilga flowing past landfill sites of leachate at the Cracow Soda Works, where these anions were measured by ion chromatography. Results demonstrated, from 4 sampling points along a 3 km stretch, an over tenfold increase in chlorides, with the greatest rise seen between the third and fourth points. Levels of nitrates and sulphates however, did not significantly increase [23].

A study by *Wiśniowska-Kielian* and *Niemiec* [22] with 5 water sampling points along the Dunajec river (of which 3 were after stream estuaries from irrigating agricultural land) measured nitrate-nitrogen using spectrophotometry. They showed large variations between the times of sampling as well as between the sampling points, where the results from the first and last points proved similar, whilst those intermediate showed fourfold differences. Such results thus showing how very useful monitoring can be at selected stretches of rivers that are subjected to strong anthropic pressure.

Defining sampling points, separated by fairly close distances, permits an accurate estimation to be made on the water quality grades of surface waters at chosen sections of a running watercourse, thereby allowing sources of pollution to become identified. Limiting values for water quality grades are defined in the regulations set by the Ministry of the Environment [15] and for chlorides, at Class I and II, are respectively 200 and 300 mg/L, for sulphates respectively 150 and 250 mg/L, and respectively 2.2 and 5.0 mg/L for nitrate-nitrogen. The presented study demonstrates that these levels were exceeded only for nitrate-nitrogen, but not for chlorides nor sulphates; Table 2.

Table 2. Exceedances of nitrate-nitrogen limits in watercourse samples

| | Point 1 | Point 2 | Point 3 | Point 4 | Point 5 | Point 6 |
|---|---|---|---|---|---|---|
| Watercourse in Niwiska | | | | | | |
| Wisłok | | | | | | |
| Mleczka | | | | | | |
| San | | | | | | |
| Bystrzyca | | | | | | |
| Nil | | | | | | |

Legend:
Coloured white – waters meeting the nitrate-nitrogen requirements set out in the Class I limit values.
Coloured gray - waters that exceed nitrate-nitrogen requirements set out in the Class I limit values (2.2 mg/L).
Coloured black – waters that exceed nitrate-nitrogen requirements set out in the Class II limit values (5.0 mg/L).

## CONCLUSIONS

1. The most obvious effect that urban settlements have on watercourses was observed in their flowing through the small and medium sized towns of Kolbuszowa, Przeworsk and Jaroslaw.
2. The effect of urban environmental impact is most frequently seen by increased chlorides in the municipal wastewater.
3. Water sampling should be made at several points, situated along those watercourses coming under anthropic pressure, by which means the sources of pollution can be identified, eg. illegal discharges of sewage or industrial waste into rivers. Appropriate remedial measures can thus also be introduced.
4. Ion chromatography has proved a useful method for estimating the urban environmental impact on watercourses by measuring anion concentrations.

**Conflict of interest**
*The authors declare no conflict of interest.*

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