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### Abstract

Santiago del Estero is a province located in northwestern Argentina. The Dulce River is used for irrigation through a vast network of channels and ditches, including the San Martin Canal (SMC), which crosses the capital city of Santiago del Estero. This canal's water is used for drinking, as well as recreational use for the general population. However, this river has been seriously polluted for several decades. The present study focuses on the identification and the quantification of the water pollution levels of total phenols in the SMC according to the seasonal periods. Water samples from various areas of the canal in different months of the year, extending from December to September, were collected for analysis. Additionally, the concentration of total dissolved solids (TDS), chlorides, sulphates, nitrites and organic matter, as well as water hardness and alkalinity, were analysed in order to conduct a more complete study of the contamination of this area. The results showed a worrying total phenol concentration that exceeded the limit set by Argentine legislation for drinking water, as well as water for recreational use ( $5 \text{ } \mu\text{g/L}$ ). The total phenol (TP) concentration was directly determined by a molecular absorption spectroscopy method based on a new flow injection analysis system (FIA). Under the selected experimental conditions, the detection and quantification limits were  $0.0490$  and  $0.1633 \text{ } \mu\text{g/mL}$ , respectively. The developed method provides a number of improvements related to the speed of analysis, the restricted consumption of the reagents and sample volumes and the unnecessary sample treatment that contribute to environmentally friendly analytical chemistry. The results showed that TP make a significant contribution in the SMC pollution, especially during the months of April ( $400 \pm 110 \text{ } \mu\text{g/L}$ ) and September ( $240 \pm 20 \text{ } \mu\text{g/L}$ ). A high sulphate concentration that was higher than the limit allowed by the legislation was also found.

<b>Keywords</b>	San Martin Canal pollution; Phenols; Flow injection analysis; Human health risks; Spectrophotometry
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1 **EVALUATION OF TOTAL PHENOL POLLUTION IN WATER OF SAN MARTIN**  
2 **CANAL FROM SANTIAGO DEL ESTERO, ARGENTINA**

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25 **Abstract**

26 Santiago del Estero is a province located in northwestern Argentina. The Dulce  
27 River is used for irrigation through a vast network of channels and ditches, including  
28 the San Martin Canal (SMC), which crosses the capital city of Santiago del Estero.  
29 This canal's water is used for drinking, as well as recreational use for the general  
30 population. However, this river has been seriously polluted for several decades.

31 The present study focuses on the identification and the quantification of the  
32 water pollution levels of total phenols in the San Martin Canal according to the  
33 seasonal periods. Water samples from various areas of the canal in different months  
34 of the year, extending from December to September, were collected for analysis.  
35 Additionally, the concentration of total dissolved solids (TDS), chlorides, sulphates,  
36 nitrites, and organic matter, as well as water hardness and alkalinity, were analysed  
37 in order to conduct a more complete study of the contamination of this area. The  
38 results showed a worrying total phenol concentration that exceeded the limit set by  
39 Argentine legislation for drinking water, as well as water for recreational use (5  
40  $\mu\text{g/L}$ ). The total phenol (TP) concentration was directly determined by a molecular  
41 absorption spectroscopy method based on a new flow injection analysis system  
42 (FIA). Under the selected experimental conditions, the detection and quantification limits  
43 were 0.0490 and 0.1633  $\mu\text{g/mL}$ , respectively. The developed method provides a  
44 number of improvements related to the speed of analysis, the restricted  
45 consumption of the reagents and sample volumes and the unnecessary sample  
46 treatment that contribute to environmentally friendly analytical chemistry. The  
47 results showed that TP make a significant contribution in the San Martin Canal  
48 pollution, especially during the months of April ( $400 \pm 110 \mu\text{g/L}$ ) and September

49 (240 ± 20 µg/L). A high sulphate concentration that was higher than the limit  
50 allowed by the legislation was also found.

51 Capsule: The total phenols content in the San Martin Canal water in its route  
52 through the city of Santiago del Estero is the limit established by the current  
53 legislation.

54

55 **Keywords:** San Martin Canal pollution; Phenols; Flow injection analysis; Human  
56 health risks; Spectrophotometry

57

## 58 **1. Introduction**

59 The Dulce River, the most important river in the Argentine province of  
60 Santiago del Estero, begins in the Tucumán Province. Derivation channels and  
61 ditches, including the San Martin Canal (SMC), have been constructed to enable  
62 integral and permanent use of the waters of the Rio Dulce, to overcome the  
63 limitations of seasonal irrigation and the salinization of the soils and to add  
64 thousands of hectares to the agriculturally productive area of the province. The SMC  
65 crosses the city of Santiago del Estero (capital of the province of Santiago del Estero)  
66 from north to south, passing through the urban agglomerate that forms the city of  
67 Santiago del Estero. Consequently, the canal receives a high wastewater load from  
68 these densely populated zones that affects the water quality and could be associated  
69 with a wide range of diseases affecting the inhabitants of the surrounding areas.

70 The San Martin Canal passes through urbanized areas and is widely used for  
71 recreational activities. In certain cases, in hot weather, the water of the SMC is also  
72 used for consumption. To the best of our knowledge, there have been no studies that  
73 provide data and information regarding about the quality and usability of the water

74 of the canal. In this regard, there are no warnings for the residents regarding the use  
75 of this water, particularly for children who use the canal water for swimming.

76 Growing attention has been directed at organic compounds, such as total  
77 phenols, which were detected in the San Martin Canal due to their different toxicity  
78 levels and cause a rather offensive taste and odours. Generally, these types of  
79 compounds are present in the atmosphere and usually come from natural sources  
80 as a result of the decomposition of organic matter (4 per cent of the total phenols)  
81 or anthropogenic activity (96 per cent of the total phenols) (Cooper et al., 1996;  
82 Campos, 2009). Total phenols are released by a large number of industries, such as  
83 oil refining, petrochemical plastic and paper manufacturing, and steel industries,  
84 and due to the use of insecticides containing toxic nitrophenols in agriculture  
85 (Christophersen and Catdwell, 1996). Phenols occur frequently in a wide range of  
86 natural waters and industrial wastes and their analysis and control is of prime  
87 importance owing to their persistence, toxicity and bioconcentration capacity not  
88 only in water but also in soil, food, and terrestrial and marine animals (Steinberg,  
89 1998; Liu et al., 2012). Most of the phenols released into the environment go into  
90 water (73.3 per cent of the total phenols of anthropogenic origin), 26.3 per cent  
91 remain in the air and approximately 0.4 per cent stay in the soil and aquatic  
92 sediments (Christophersen and Catdwell, 1996).

93 Various health organizations, such as the *International Agency for Research on*  
94 *Cancer* (IARC), *Environmental Protection Agency* (EPA) and *Agency for Toxic*  
95 *Substances and Disease Registry* (ATSDR, 2008) have indicated that phenol  
96 carcinogenicity in humans cannot be classified to date (Depetris et al., 2010).  
97 However, it has been clearly demonstrated that these compounds show quick  
98 absorption by inhalation, skin contact and by ingestion and their vapours may be

99 corrosive on contact with eyes, skin and respiratory tract, as well as affecting the  
100 digestive system. The EPA established the maximum phenol concentration level of  
101 0.006 µg/L over a period to up 10 days, which does not cause adverse effects or  
102 0.002 µg/L for lifetime exposure (ATSDR, 2008). The Argentine environmental  
103 legislation concerning the total phenols (TP) concentration is more restrictive. The  
104 Ministry of Environment Sustainable Development of the Nation, by the Regulatory  
105 Decree 831/93 of Law 24051 (DR 831/93), established 1.0 µg/L as the TP guiding  
106 level in fresh surface waters for the protection of aquatic life and 5.0 µg/L in water  
107 for recreational use. Owing to the above mentioned legislation that regulates the  
108 maximum TP level permissible in water, methods that enable strict control of the TP  
109 concentration are necessary. For these reasons, legislation has been enacted  
110 nationally and internationally to control the maximum TP levels permissible in  
111 water.

112         There have been several published reports regarding the methods for the  
113 determination of TP content in water. However, most of the reported methods have  
114 high detection limits, and require high sample volumes and sample processing  
115 (Eisapour et al., 2012; Lavilla et al., 2012; Sousa et al., 2009). Dollato et al. have  
116 developed an online method using a low sample volume, but this method exhibits a  
117 high limit of detection (LOD) (Dolatto et al., 2012). To date, there has been no  
118 continuous monitoring of the possible contamination of the water of the canal by TP  
119 compounds, nor is it known how this pollution can vary according to the season.

120         The aim of this work is to identify and determine the patterns of water  
121 pollution due to TP in different areas of the San Martin Canal and for different  
122 seasonal periods, which can affect the human health of a significant population  
123 group in the city of Santiago del Estero such that the relevant authorities can take

124 protective measures against the pollution according to the established law. In this  
125 study, the determination of nitrites was carried out by a simple spectrophotometric  
126 method, previously developed by our research group (López Pasquali et al., 2007).  
127 Physical and chemical parameters were determined by established reference  
128 methods. In addition, to address the most important problem related to phenols  
129 contamination, we proposed a new, simple and environmentally friendly  
130 spectrophotometric method based on a flow injection analysis system for the  
131 determination of total phenols (TP) in the water samples of the San Martin Canal.  
132 The developed method does not need prior sample treatment, is faster than the  
133 method reported in the literature, and consumes less sample volume than other  
134 standard methods. This method is a low-cost approach and could be used in  
135 environmental laboratories that cannot use expensive instrumentation.

136

## 137 **2. Materials and Methods**

### 138 *2.1. Sample collection*

139 To evaluate the potential pollution of the San Martin Canal (SMC), this study  
140 analysed a total of 200 real water samples from this canal along the complete route  
141 of the river through the City Santiago del Estero (Fig. 1). Water was sampled at 5  
142 points of interest located in various sites along the San Martin Canal, with 10  
143 samples being taken at each point to be analysed. The samples collected at point 1  
144 are obtained from the origin of the San Martin Canal from the Rio Dulce. Samples of  
145 points 2, 3 and 4 correspond to the more urbanized areas in the centre of the city,  
146 while the samples of point 5 were taken at the end of the San Martin Canal in the  
147 area with a lower population density in the capital. In addition, the sampling was

148 performed during different seasons such as summer, autumn and spring. The  
149 samples were analysed within 24 - 48 hours of collection.

150 The collection of the samples at the five points was carried out following the  
151 Standard UNE-EN 25667-2 (UNE-EN 25667-2, 1995). In this study, topaz glass  
152 bottles, previously washed and dried at 60 °C in an oven, were used as total phenols  
153 containers. Plastic bottles were also employed as containers to store the samples  
154 and to analyse other parameters.

155

## 156 2.2. Chemicals

157 All chemicals used in this work were analytical grade and were supplied by  
158 Biopack (Buenos Aires, Argentina. Powered by Clarity S.A). The solutions were  
159 prepared using ultra-pure deionized water obtained using a GT Lab water  
160 purification system (Rosario, Argentina), which resulted in the water resistivity of  
161 at least 18 MΩ/cm.

162 For TP analysis, the stock standard solution of phenol at 1000 µg/mL was  
163 prepared by dissolving the adequate amount of phenol in water and storing at 4°C  
164 until use. To prepare the calibration curve, working standard solutions at adequate  
165 concentration in the range between 0.10 to 32 µg/mL were prepared daily by  
166 appropriate dilution of the mentioned solution with deionised water.

167 Carrier solution (CS) was prepared by mixing 1.0 g potassium ferricyanide, 20  
168 g of potassium sodium tartrate tetrahydrate, 3.4 g ammonium chloride and 2.05 g  
169 ammonium hydroxide in a volume of 100 mL of water, and adjusting the pH to 10. A  
170 colourimetric reagent solution (CR) of 4-aminoantipyrine (4-AAP) at 2% (w/v) was  
171 prepared adding 0.5 g to 25 mL water.

172



173 2.3. *Analytical procedures*

174 ***Flow injection system***

175 A schematic diagram of the flow injection system (FIA) used for on-line total  
176 phenols determination is shown in Figure 2. The phenolic compounds can react with  
177 4-aminoantipyrine (4-AAP) at basic pH in the presence of potassium ferricyanide,  
178 giving rise to the formation in several seconds of a coloured antipyrin compound  
179 (Fig. 2), which can be determined by spectrophotometry at 510 nm. The procedure  
180 was as follows: a Gibson Minipuls 3 peristaltic pump was used to drive all solutions  
181 through the system to the detector. The sample solution (S) was injected from a  
182 Rheodyne 5020 injection valve (six-way) into the carrier solution (CS) and mixed in  
183 the first reaction coil (C1). The colourimetric reagent (CR) was pumped from a  
184 different pump channel and mixed with the sample in the second reaction coil (C2).  
185 Next, the developed colour was measured in the flow cell in the spectrophotometer  
186 Spectrum SP 2000 UV. Teflon pieces and tubing (0.8 mm i.d) were used as  
187 connectors.

188 ***Total phenol determination***

189 All collected samples were filtered prior to the analysis. A volume of 240  $\mu\text{L}$  of  
190 different samples (S) was injected into the carrier solution (CS) at the flow rate of  
191 1.20 mL/min, and the colourimetric reagent (CR) was pumped at the rate of 0.32  
192 mL/min. After the reaction in both coils, the coloured complex passed to the flow  
193 cell for the measurements of the spectrophotometric signal at 510 nm. The sample  
194 concentration was extrapolated from the calibration graph (0.1 to 32  $\mu\text{g/mL}$  of  
195 phenol) using the same procedure. To avoid the biochemical oxidation of phenolic  
196 compounds, the samples were analysed within four hours of collection.

197

198 ***Other parameter determination***

199 Different possible pollutants that could affect the water quality characteristics  
200 of the San Martin Canal such as total dissolved solids (TDS), chlorides, sulphates,  
201 alkalinity and hardness were analysed by standard methods (APHA, AWWA, WEF,  
202 2012).

203 The pH measurements were performed using a magnetic stirrer model 78 HW-  
204 1 and an OAKTON Ion 510 series pH metre. A Franklin thermometer (Industrial  
205 Argentine) was used for room and water temperature measurements.

206 The determination of nitrites was carried out by a spectrophotometric flow  
207 injection analysis method (López Pasquali et al., 2007). The organic matter content  
208 of the water samples was analysed by the permanganate oxidation process (Panreac  
209 Quimica, S.A., 2000), which is eco-friendly and has gained importance in green  
210 chemistry.

211

212 *2.4. Validation method*

213 The proposed method was validated for the detection and quantification limits,  
214 linearity and precision under the optimum conditions for spiking water samples.  
215 The calibration curve was plotted in the range of 0.1 to 32 µg/mL using the data in  
216 triplicate. The detection and quantification limits were calculated by the UPAC  
217 method. Precision was estimated from the relative standards of five successive  
218 injections of the samples containing phenols at three different concentrations. The  
219 developed FIA method was also validated by the comparison with the standard  
220 manual method (APHA, AWWA, WEF, 2012). For this purpose, the t-test was  
221 applied.

222

## 223 2.5. Data analysis

224 The optimizations of the physical and chemical parameters of the FIA system  
225 were carried out by the univariate statistical method (Reis et al., 1994) and the  
226 variable-size simplex method (Nelder et al., 1965). For these optimizations, all  
227 measurements were performed in triplicate.

228 All analytical determinations of the study (e.g., TP, OM, TDS, chlorides,  
229 sulphates, and nitrates) were performed by taking 10 canal water samples at each  
230 sampling point and in different seasons of the year.

231 All analyses were performed on the day of the sampling and within four hours  
232 of samples collection.

233

## 234 3. Results and Discussion

### 235 3.1. Optimization method for total phenol determination

236 To identify the best conditions to for the determination of the TP  
237 contamination by the proposed FIA method, the physical and chemical parameters  
238 affecting the operation procedure were optimized. The influence of the differences  
239 in the concentrations of the components of the carrier solution was studied. The  
240 composition of the carrier solution was optimized by varying the amounts of  
241 ferricyanide (5 - 10 g), potassium sodium tartrate tetrahydrate (50 - 200 g/L) and  
242 ammonium chloride and ammonium hydroxide (5 - 15 g/L). The maximum  
243 analytical signal is reached for 6 g/L of potassium ferricyanide, 175 g/L of potassium  
244 sodium tartrate tetrahydrate, 20 g/L of ammonium chloride and 10 g/L ammonium  
245 hydroxide. The effect of the colourimetric reagent (4-AAP) concentration was  
246 evaluated by varying the concentration of 4-AAP from 5 to 20 g/L. The obtained

247 results indicate that the highest analytical response was observed for 4-AAP at the  
248 concentration of 17.5 g/L.

249 Physical variables, such as the flow rate of each reactant in the flow system,  
250 were optimised by the univariate method in the range from 0.5 to 3 mL/min. As a  
251 compromise between the measurement time and sensitivity, the flow rates of 1.60,  
252 1.20 and 0.32 mL/min were chosen for the water sample (S), carrier solution (CS)  
253 and colourimetric reagent (CR), respectively. Other physical parameters such as the  
254 sample injection volume and lengths of the reaction coils 1 (volume 402  $\mu$ L) and 2  
255 (volume 151  $\mu$ L) were optimized using the variable-size simplex method at  $\lambda = 510$   
256 nm when a phenol solution of 1.0  $\mu$ g/mL was injected. Figure 3 represents the  
257 response values plotted against each vertex obtained by applying the Simplex  
258 method. Initially, the response values were low and fluctuated considerably until a  
259 much lower variation was achieved with higher values allowing the optimum  
260 conditions to be defined. The optimal response was obtained for vertices 16 and 20,  
261 the coordinates of which correspond to the injection volume of 240  $\mu$ L, and the  
262 lengths of reaction coils 1 and 2 of 0.80 and 0.30 m, respectively. Table 1 presents  
263 the optimum values found for the proposed FIA system. Under the optimised  
264 conditions, the sampling speed of 70 samples per hour was obtained.

### 265 *3.2. Validation method*

266 The analytical performance of the system was evaluated in terms of the  
267 detection and quantification limits, linear range and precision. To establish the  
268 linearity range of the proposed method, the calibration curve between 0.1 and 32  
269  $\mu$ g/mL was evaluated, obtaining the linearity range of 0.08 to 35  $\mu$ g/mL with the  
270 limit of detection (LOD) of 0.049  $\mu$ g/mL and the limit of quantification (LOQ) of

271 0.163 µg/mL. Precision was calculated at three different concentrations (0.5, 15 and  
272 30 µg/mL) in terms of the relative standard deviation values, and the obtained  
273 values were in the range of 0.81% to 1.26%. To calculate the limit of detection, the  
274 Miller equation: Limit of detection =  $y_B + 3S_B$  (Miller et al., 2000) was used based on  
275 the values obtained from the linear regression analysis, calculated as recommended  
276 by the IUPAC (LOD =  $3S_B/m$ , where  $m$  is the slope of the calibration graph).

277 The influence of different interfering substances (NaCl,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_2^-$ , Fe  
278 (total),  $\text{Al}^{3+}$  and  $\text{Cu}^{2+}$ ) was studied by adding variable amounts of these compounds  
279 to the solutions with phenol concentration of 1 µg/mL. No analytical signal variation  
280 was observed using NaCl 4000 µg/mL,  $\text{NO}_3^-$  720 µg/mL,  $\text{NO}_2^-$  1.60 µg/mL,  $\text{SO}_4^{2-}$  1600  
281 µg/mL, Fe 4.80 µg/mL,  $\text{Al}^{3+}$  1.60 µg/mL and  $\text{Cu}^{2+}$  8 µg/mL, as maximum  
282 concentrations. These results indicate that **there is no interference of these**  
283 **substances when determining the TP content by the proposed method at the TP**  
284 **concentration of 1 µg/L.**

285 To validate the results obtained by the proposed FIA method, five SMC samples  
286 were simultaneously analysed by the standard manual method (APHA, AWWA,  
287 WEF, 2012). The t-test was applied, obtaining experimental values lower than the  
288 critical value. As shown in Table 2, no significant differences between the standard  
289 method and the proposed FIA method were found working at the significance level  
290 of approximately 50% ( $p = 0.49$ ), indicating the validity of the method for the  
291 determination of the TP content in the water samples from the SMC.

292

### 293 *3.3. Total phenol and pollutant content in waters of SMC*

294 The optimized and validated FIA method was used to determine the total  
295 phenols in the water of SMC. In addition, different physical and chemical parameters

296 such as pH, temperature, alkalinity, hardness, organic matter content (OM), total  
297 dissolved solids (TDS), chloride, nitrates and sulphates in channel waters were also  
298 determined. Table 3 presents the values for all physical and chemical parameters  
299 obtained using ten samples at the five sampling points, taken over 4 months in  
300 different seasons.

301 Ambient and water temperatures were consistent with the seasons of the year.  
302 According to the alkalinity values found in the samples, the pH remained in the range  
303 of 8.50 to 7.51, (Fig. 4). TDS content shows the highest value in December, decreases  
304 in February and April, and increases slightly in September. The results of the  
305 evaluation of TD, chloride, sulphate and nitrite contents are shown in Figure 5. The  
306 values obtained for chloride are similar in all samples, with a slight increase during  
307 February but are far from the limit allowed by the current legislation in water (350  
308  $\mu\text{g}/\text{mL}$  according to the legislation (C.A.A., 2017)). A similar situation is observed  
309 for hardness and alkalinity, where the highest values are found in February.

310 Sulphates are present in concentrations not exceeding 207  $\mu\text{g}/\text{mL}$ , below the  
311 limit of 400  $\mu\text{g}/\text{mL}$  fixed for water by legislation (C.A.A., 2017). Only in February a  
312 contamination with nitrites is observed, which coincides with the high temperatures  
313 and the intensive use of the canal for recreation.

314 All analysed samples showed quite high OM values. The values vary in the the  
315 4.0-6.0  $\mu\text{g}/\text{mL}$  range, indicating that the water quality is poor. The presence of the  
316 OM could increase the values of TP present in the water as shown in Figure 6. **The**  
317 **amounts of TP and OM are related because total phenols are generated by the**  
318 **degradation of the organic matter and phenolic acids result from the breakdown of**  
319 **humic acids.**

320 The concentrations obtained for TP are plotted in Figure 6 for each site and  
321 month of sampling. The behaviour of the TP content is similar to the behaviour of  
322 the OM content for all samples at different months, with the highest values being in  
323 in April, and the minimum values being in February. This behaviour could be related  
324 to the ambient and water temperatures, because in February the temperature is  
325 higher, implying a greater evaporation of the phenols present in the water, whereas  
326 in April the evaporation would be lower. Likewise, it can be seen that samples 2, 3  
327 and 4 present the highest TP contents, probably owing to their proximity to the  
328 areas with higher population density.

329 All values obtained far exceed the limits of 1 and 5  $\mu\text{g/L}$  set for TP by  
330 Regulatory Decree 831/93 of Law 24051 (DR 831/93) for fresh surface water and  
331 water for recreational use, respectively. This clearly indicates a serious  
332 contamination of the waters of the San Martin Canal by phenols.

333

#### 334 **4. Conclusions**

335 A complete study investigated the organic pollution and the seasonal  
336 variability of physical and chemical parameters affecting the different areas of the  
337 San Martin Canal. A novel, simple and reliable colourimetric FIA method for the  
338 determination of total phenols content in water samples from the San Martin Canal  
339 was proposed. This methodology allows the TP monitoring using small-volume  
340 samples (240  $\mu\text{L}$ ) without the interferences by other species that can be present in  
341 the water, shows a high sampling frequency (70 samples/hour) and does not  
342 require a prior sample extraction stage. The proposed method could be considered  
343 a low-cost approach and provides a high-throughput alternative when sophisticated  
344 instrumentation is not available.

345           Based on the obtained results, it can be concluded that certain physical and  
346 chemical parameters related to the water quality of the SMC do not comply with the  
347 limits allowed by the current legislation for water consumption and recreation.  
348 The presence of organic matter and phenols in canal waters observed in the four  
349 periods analysed implies that this water is not appropriate for consumption or  
350 recreation. The results showed average total phenol concentration in water is higher  
351 in April and September and in the higher population density areas. We highlight that  
352 the Canal contamination due to these compounds exceeded the limit set by the  
353 legislation (5 µg/L TP) in all cases. The presented results invite particular attention  
354 to the organic matter and total phenol content contamination of San Martin Canal  
355 water on its way through the city of Santiago del Estero that can negatively impact  
356 the surrounding environment and the health of the population, especially the elderly  
357 and children who use this water for recreation and swimming. This study also  
358 enabled us to establish a conceptual pollution scheme that may facilitate better  
359 contamination management by government authorities through the identification  
360 of the area and the seasonal period when the risk of canal is maximal, allowing a  
361 sampling design or providing attention to water treatment.

362           The conclusions obtained in this work have led to an important discussion.  
363 The discussion has spread all over the country to the point that the government is  
364 aware of the need to take corrective measures for the worrying pollution situation  
365 of the Dulce River. In fact, government authorities have urged Tucuman industry to  
366 treat their effluents before disposing of them into the rivers.

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368

369



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452 **Figure captions**

453 Figure 1. Geographic location of San Martin Canal in the city of Santiago del Estero  
454 belonging to the Santiago del Estero Province (Argentina). Geographic distribution of  
455 water sites in the San Martin Canal.

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457 Figure 2. Flow injection system scheme for total phenols analysis. S: sample, CS: carrier  
458 solution, CR: colourimetric reagent (4-aminoantipyrine in water), C1 and C2: first and  
459 second reactors.

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461 Figure 3. Response improvement as a function of the vertex number for phenol during  
462 simplex search.

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464 Figure 4. pH and alkalinity values found in SMC during the entire period studied.

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466 Figure 5. Total dissolved solids (TDS), chloride, sulphate and nitrite contents  
467 measured in water samples of SMC according to the seasonal periods studied.

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469 Figure 6. Total phenol (TP) and organic material (OM) contents measured in water  
470 samples of SMC according to the seasonal periods studied.

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485 **Tables**

486

487 Table 1. Optimum conditions for the proposed FIA system.

488

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490 standard method and by the proposed FIA method.

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493 water samples for five sites (n= 10) in the different seasonal periods studied.

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Variable		Optimum value
Carrier solution (CS) (g/L)	Potassium ferrocyanide	6
	Potassium sodium tartrate	175
	Ammonium chloride	20
	Ammonia	10
Colourimetric reagent (CR) (g/L)	4-aminoantipyridine	17.5
Flow rate (mL/min)	Sample (S)	1.60
	Carrier solution (CS)	1.20
	Colourimetric reagent (CR)	0.32
Injection volume ( $\mu$ L)		240
Reaction coil length (m)	Reaction coil with CS (C1)	0.8
	Reaction coil with RS (C2)	0.3

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502 Table 2. Results obtained for the total phenol determination of five samples by the  
503 standard method and the proposed FIA method.

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Sampling	Phenol standard method ( $\mu\text{g/mL}$ )	RSD (%)	Phenol proposed FIA method ( $\mu\text{g/mL}$ )	RSD (%)
1	$0.82 \pm 0.02$	2.19	$0.88 \pm 0.01$	1.14
2	$1.07 \pm 0.02$	2.16	$1.09 \pm 0.01$	0.92
3	$1.68 \pm 0.02$	1.43	$1.64 \pm 0.01$	0.61
4	$1.04 \pm 0.02$	1.92	$1.02 \pm 0.01$	0.98
5	$0.93 \pm 0.02$	2.15	$0.93 \pm 0.01$	1.07

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Table 3. Means and standard deviation values for physical and chemical parameters analysed in the SMC water samples for five sites in the different seasonal periods studied.

Parameters	Site 1*				Site 2*				Site 3*				Site 4*				Site 5*			
	Dec	Feb	Apr	Sept	Dec	Feb	Apr	Sept	Dec	Feb	Apr	Sept	Dec	Feb	Apr	Sept	Dec	Feb	Apr	Sept
Room Temp (°C)	35.0 ± 0.5	42.0 ± 0.5	27.0 ± 0.5	28.0 ± 0.5	36.8 ± 0.5	35.5 ± 0.5	28.0 ± 0.5	29.0 ± 0.5	45.0 ± 0.5	36.0 ± 0.5	28.0 ± 0.5	29.0 ± 0.5	35.0 ± 0.5	36.0 ± 0.5	28.0 ± 0.5	29.0 ± 0.5	35.0 ± 0.5	36.0 ± 0.5	28.0 ± 0.5	29.0 ± 0.5
Water Temp (°C)	30.0 ± 0.5	32.0 ± 0.5	21.0 ± 0.5	23.0 ± 0.5	43 ± 0.5	26.5 ± 0.5	22.0 ± 0.5	23.0 ± 0.5	35.5 ± 0.5	26.0 ± 0.5	22.0 ± 0.5	24.0 ± 0.5	45.0 ± 0.5	27.0 ± 0.5	22.0 ± 0.5	24.0 ± 0.5	45.5 ± 0.5	27.0 ± 0.5	22.0 ± 0.5	24.0 ± 0.5
pH	8.38 ± 0.01	7.92 ± 0.01	7.64 ± 0.01	7.71 ± 0.01	8.50 ± 0.01	7.90 ± 0.01	7.54 ± 0.01	7.80 ± 0.01	8.50 ± 0.01	8.10 ± 0.01	7.51 ± 0.01	7.73 ± 0.01	8.24 ± 0.01	7.80 ± 0.01	7.58 ± 0.01	7.78 ± 0.01	8.38 ± 0.01	7.80 ± 0.01	7.55 ± 0.01	7.82 ± 0.01
TDS (µg/mL)	333.5 ± 10.4	221.5 ± 12.7	232.0 ± 11.0	270.5 ± 11.9	322.0 ± 12.4	221.5 ± 12.7	226.5 ± 14.3	265.0 ± 14.1	296.0 ± 15.0	213.5 ± 11.8	229.0 ± 13.9	268.0 ± 16.6	341.5 ± 22.8	219.5 ± 13.2	228.0 ± 12.9	265.5 ± 17.1	319.0 ± 15.0	217.0 ± 13.6	224.0 ± 14.4	270.0 ± 20.3
chlorides (µg/mL)	59.00 ± 3.80	59.64 ± 4.20	55.38 ± 3.20	46.15 ± 2.90	57.5 ± 3.70	59.64 ± 3.30	53.96 ± 4.8	43.15 ± 2.90	58.2 ± 3.70	59.64 ± 3.60	53.96 ± 3.10	47.57 ± 2.10	58.2 ± 4.00	58.22 ± 4.30	55.38 ± 3.70	45.44 ± 2.20	58.2 ± 4.10	58.2 ± 4.30	56.8 ± 3.70	46.86 ± 2.80
Hardness (µg/mL)	180 ± 15	125 ± 11	115 ± 10	140 ± 13	160 ± 13	100 ± 10	115 ± 11	110 ± 10	160 ± 14	100 ± 11	100 ± 10	130 ± 12	160 ± 14	100 ± 11	120 ± 11	130 ± 12	160 ± 14	100 ± 10	120 ± 12	120 ± 12
Alkalinity (µg/mL)	360 ± 15	360 ± 13	220 ± 12	280 ± 13	400 ± 16	360 ± 13	220 ± 11	320 ± 12	400 ± 14	360 ± 13	240 ± 11	320 ± 13	360 ± 14	360 ± 15	240 ± 12	280 ± 14	320 ± 13	300 ± 15	240 ± 14	280 ± 13
Sulphates (µg/mL)	134.4 ± 9.5	158.4 ± 10.8	165.6 ± 12.1	172.8 ± 12.5	124.8 ± 9.2	168 ± 13.4	206.4 ± 14.8	168.0 ± 14.0	120.0 ± 9.1	168.0 ± 13.7	216.0 ± 14.0	153.6 ± 12.2	129.6 ± 10.1	165.6 ± 12.8	168.0 ± 13.5	163.2 ± 11.9	134.4 ± 10.4	163.2 ± 11.5	160.8 ± 9.8	139.0 ± 9.5
Nitrites (µg/mL)	0.070 ± 0.005	0.110 ± 0.007	0.040 ± 0.003	0.020 ± 0.003	0.050 ± 0.004	0.170 ± 0.009	0.060 ± 0.005	0.020 ± 0.004	0.050 ± 0.004	0.160 ± 0.006	0.050 ± 0.005	0.020 ± 0.003	0.040 ± 0.003	0.160 ± 0.006	0.060 ± 0.005	0.060 ± 0.004	0.040 ± 0.003	0.040 ± 0.002	0.060 ± 0.006	0.090 ± 0.008
OM (µg/mL)	5.26 ± 0.08	4.40 ± 0.06	5.36 ± 0.05	3.92 ± 0.04	5.18 ± 0.07	5.28 ± 0.07	6.08 ± 0.08	3.80 ± 0.05	5.76 ± 0.08	4.96 ± 0.06	5.76 ± 0.07	3.64 ± 0.04	4.78 ± 0.06	4.88 ± 0.07	5.68 ± 0.08	3.92 ± 0.05	3.61 ± 0.07	3.61 ± 0.06	5.52 ± 0.08	4.00 ± 0.06
TP (µg/mL)	0.160 ± 0.002	ND**	0.230 ± 0.003	0.240 ± 0.004	0.210 ± 0.003	0.130 ± 0.001	0.500 ± 0.007	0.260 ± 0.003	0.280 ± 0.005	0.060 ± 0.001	0.560 ± 0.007	0.250 ± 0.004	0.210 ± 0.003	ND**	0.440 ± 0.005	0.240 ± 0.004	0.170 ± 0.001	ND**	0.310 ± 0.003	0.210 ± 0.003

\* Average of 10 samples of each month ± standard deviation

\*\*ND: Not Detected

Fig. 1. Geographic location of San Martin Canal in the city of Santiago del Estero belonging to the Santiago del Estero Province (Argentina). Geographic distribution of water sites in the San Martin Canal.

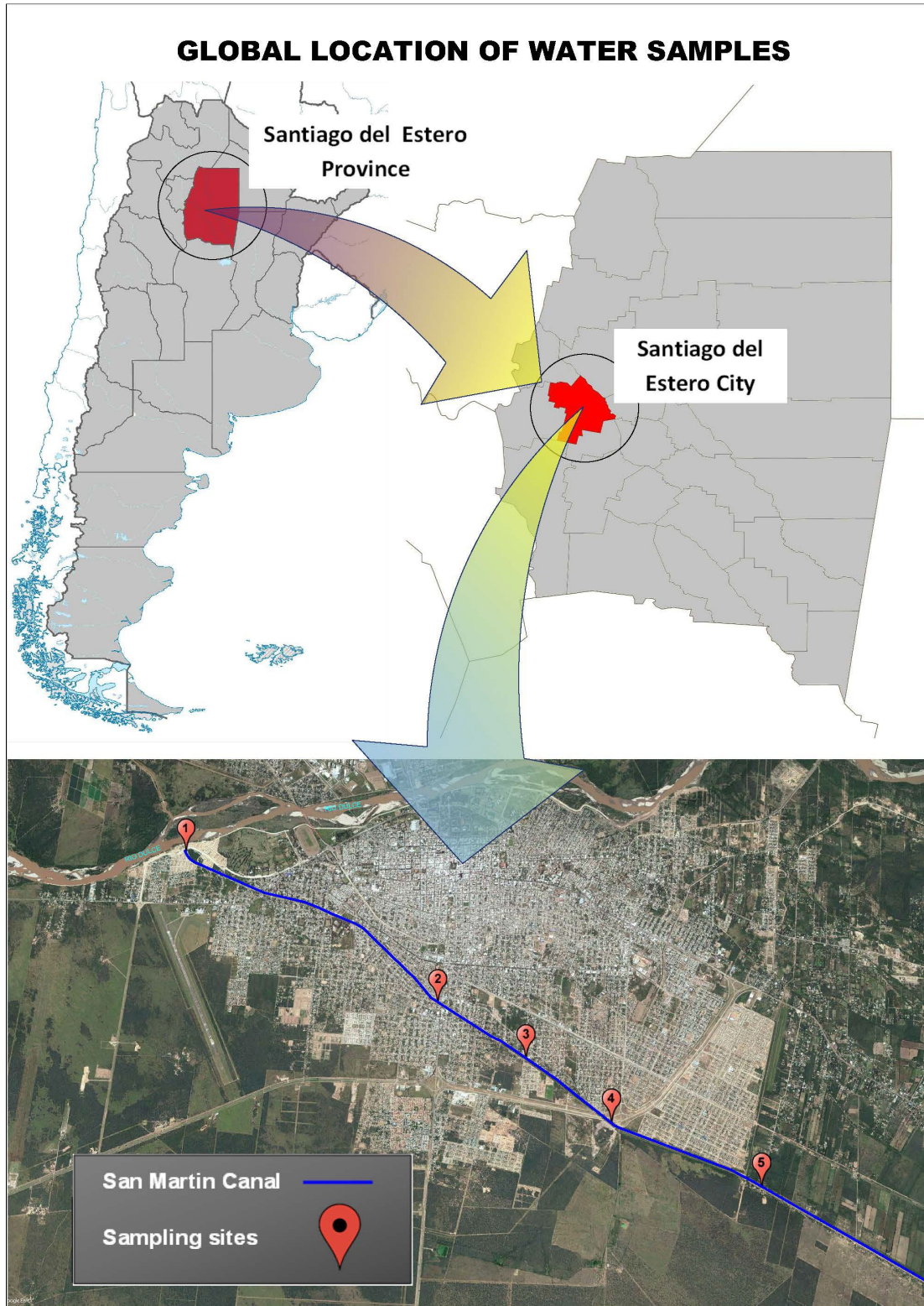


Fig. 2. Flow injection system scheme for total phenols analysis. S: sample, CS: carrier solution, CR: colourimetric reagent (4-aminoantipyrine in water), C1 and C2: first and second reactors.

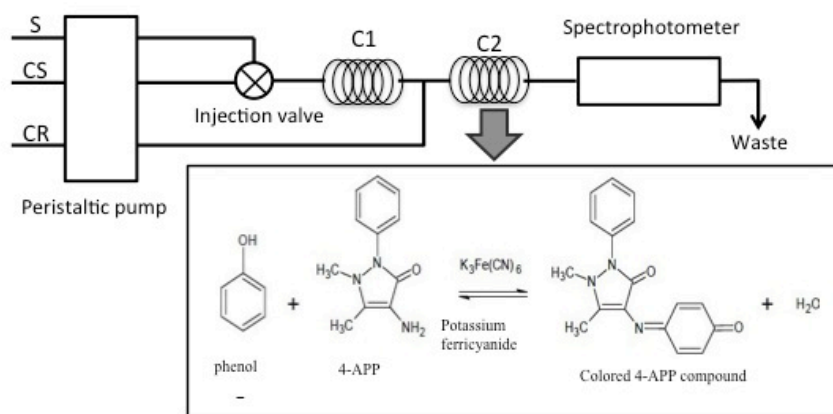


Fig. 3. Response improvement as a function of the vertex number for phenol during simplex search.

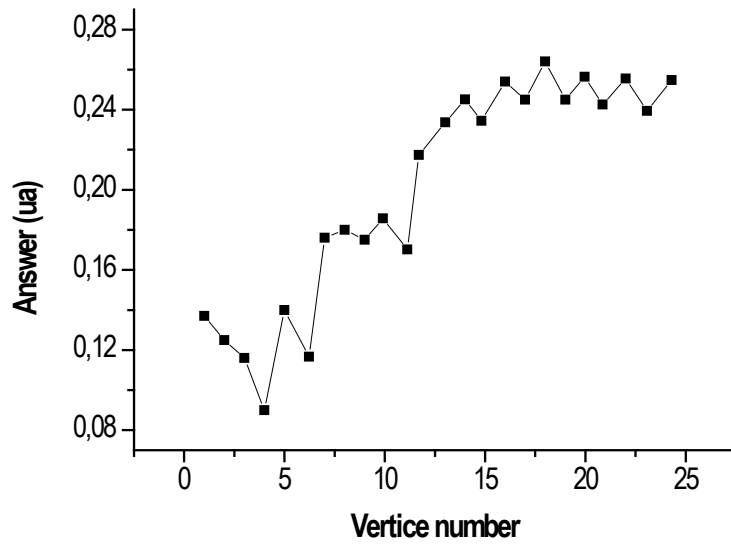


Fig. 4. pH and alkalinity values found in SMC during the entire period studied.

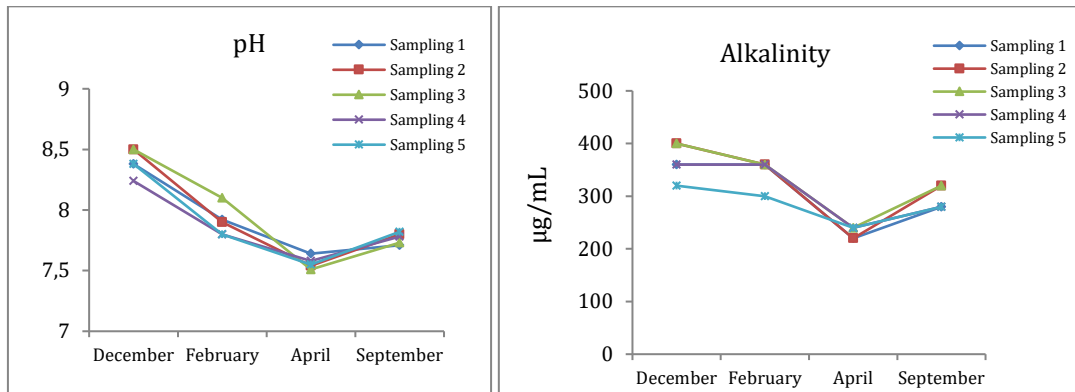


Fig. 5. Total dissolved solids (TDS), chloride, sulphate and nitrite contents measured in water samples of SMC according to the seasonal periods studied.

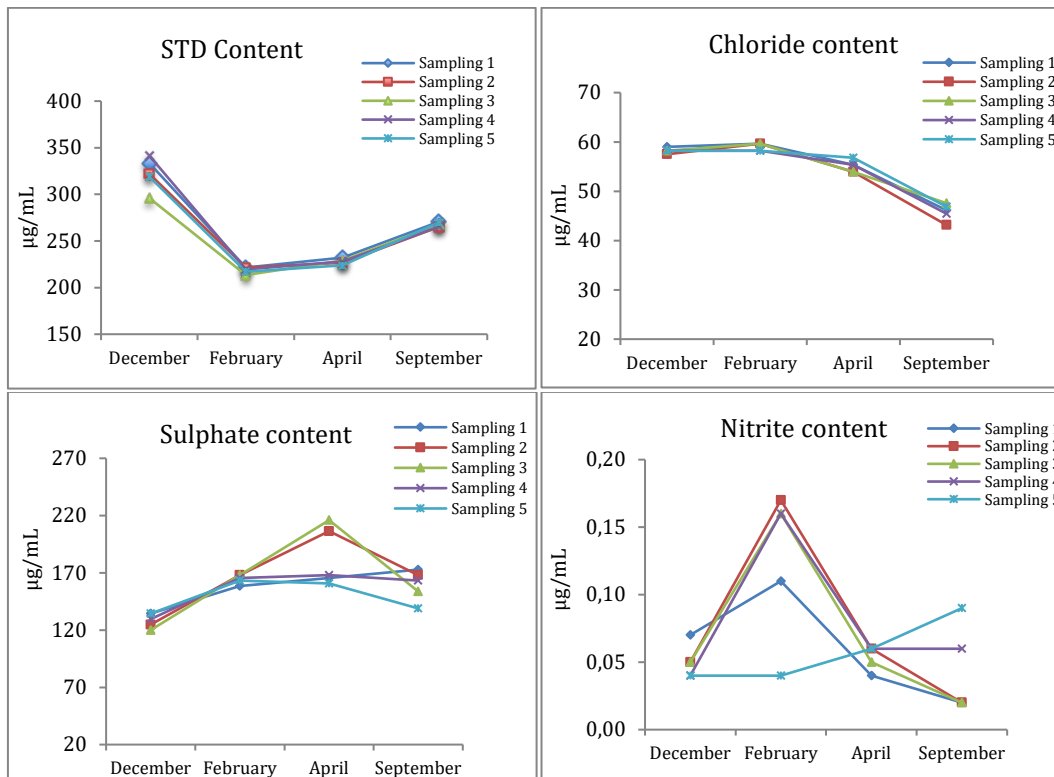


Fig. 6. Total phenol (TP) and organic material (OM) contents measured in water samples of SMC according to the seasonal periods studied.

