FACT SHEET: Po River Basin

The Po River is the longest river in Italy (661 km); it originates from Pian del Re of Monte Viso, and flows eastward till the Adriatic Sea near Venice. The Po Basin has a drainage area of 71,327 km², 70,000 km² of which are in Italy, the rest in Switzerland; 29,000 km² are on the Po plain. The basin population is close to 17 million inhabitants, almost 1/3 of the population of Italy. The main land use of the Po plain is intensive agriculture. Half of the river length is controlled by dikes to minimize flooding risk. Table 1 presents the main characteristics of the basin.
Table 1. Po River Basin characteristics

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<th>Po</th>
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<tr>
<td>COUNTRIES: ITALY, SWITZERLAND</td>
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<tr>
<td>Pedo-climate: Southern and Alpine regions; Mediterranean north, Mediterranean mountains and Alpine south zones</td>
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<tr>
<td>Drainage Area 71,327 km²</td>
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<td>Maximum altitude: 4669 m</td>
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<td>Annual average rainfall 934 mm/year</td>
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<td>Main land uses: Agriculture 41%; Forest 51%, and Urban/other 7%</td>
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<td>Population in 2015: 16,903,744</td>
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<td>River length 661 km</td>
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<td>Strahler Order – 8</td>
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<td>Discharge at outlet 1197 m³/s</td>
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<td>Outlet coordinates: 44° 57' 9&quot; N, 12° 25' 55&quot; E</td>
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About 41 % of the Po basin land use is agriculture. The Po basin hosts a large livestock population, approximately 3.1 M cattle (around 50 % of the national stock) and 6 M pigs (around 65 % of the national stock). The annual nitrate load exported from the Po River basin has increased 2–3-fold over two decades. Agriculture and livestock together contribute about 80 % of the total nitrogen load of the Po River basin, which has led to significant pressure to both surface and groundwater water bodies.

**Agriculture and water in the Po Basin**

Concentration and flows of nitrogen compounds in freshwaters associated with agriculture have increased 2–3 fold during the last decades in the Po basin (Viaroli et al., 2018). Nitrogen pollution processes from croplands to streams and aquifers can be classified in three groups: 1) winter and spring flows from upland rainfed cereal cropping systems, 2) percolation flows directly to aquifers from irrigated areas (mostly alluvial; Aschonitis et al., 2013), and 3) irrigation return flows.

Areas with high livestock density are associated with high nitrogen pollution due to over-application of manure on croplands. The application of livestock manure (pig, poultry and cattle) together with mineral fertilizers largely exceed crop uptake contributing to 85% of nitrogen reaching aquifers (Mantovi et al., 2006; Bartoli et al., 2012; Perego et al., 2012; Lasagna and De Luca, 2019). Leaching from maize is very severe and 80% of surplus can be leached (Perego et al., 2012) with a higher risk in the low-yield areas (Basso et al., 2012). Anyhow, there is high territorial diversity and in some areas such as the Volta basin in Po, good fertilization practices and the upward movement of nitrogen towards the root zone may significantly reduce nitrate leaching (Ventura et al., 2008; Morari et al., 2012). Nitrate leaching in rice is much less severe.
Phosphorous surplus has been less researched, but studies showed that the drivers controlling phosphorus pollution are 1) the type and amount of fertilization and 2) soil characteristics (Borda et al., 2010; 2011). Maxima phosphorus surpluses are originated in dairy farms, traditional farms, and pig farms. Phosphorus fertilization can, in general, be significantly reduced (Castoldi et al., 2009), also in rice fields (Zavattaro et al., 2006).

Optimized fertilization may be very effective to reduce nutrient surplus, and should encompass tuning of fertilization rates of both mineral and organic, together with the right application timing and a good knowledge of soil nutrient status (Zavattaro et al., 2006; 2012; Barbanti et al., 2006). Manure applications in areas of high animal density should be reduced, especially if the soil is left uncultivated (Mantovi et al., 2006). Lower nitrogen inputs and the right timing can reduce 33%-53% leaching but the range depends on mineral nitrogen in soils (Malik et al., 2019). Establishing a good nitrogen balance is the first step to mitigate the effect of high livestock concentration (Perego et al., 2012). Fertilization of organic and mineral sources could be reduced without affecting maize yields (Basso et al. 2012). Cocco et al. (2018) conducted a four-year lysimeter experiment to assess the impacts of shallow water table on N$_2$O emission, nitrate leaching and microbial processes for two levels of nitrogen fertilization (250 and 368 kg N/ha/y using dry manure for two years and fresh manure for the other two). The experiment used maize and six treatments (2 nitrate rates x 3 groundwater conditions - free drainage and two shallow water table levels) with replicates. When dry manure was applied, nitrate concentrations ranged from 0.005 to 4 mg NO$_3$-N/L with peaks of 28-30 mg NO$_3$-N/L. When fresh manure was applied, nitrate concentrations ranged from 0.005 to 60 mg NO$_3$-N/L for the 250 kg N/ha/y dose, and 0.05 to 196 mg NO$_3$-N/L for the 368 kg N/ha/y dose. Shallow water table favors denitrification processes, thus limiting nitrate contamination of groundwater, but at the price of higher N$_2$O emissions, a greenhouse gas being an intermediate of denitrification.

Zeolitites rock amendments can reduce the input of mineral fertilizers without affecting crop yield (Faccini et al., 2018). The use of maize silage digestate requires careful management to avoid leaching (Wysocka-Czubaszek, 2019). Increasing soil organic matter content through adequate management (including sludge) helps recover soil physical properties and improve soil fertility in the long term (Diacono and Montemurro, 2010; Fumagalli et al., 2013).

Promoting denitrification in different compartments of the system is a well-known strategy to reduce reactive nitrogen load into the system. In agricultural soils, the combination of anoxia, nitrate and labile carbon stimulate denitrification and therefore some practices such as conservation tillage or compost application have been highlighted for reducing leaching and promoting carbon sequestration. If the soil quality is improved, i.e. through compost applications, crop productivity could also be increased (Castaldelli et al., 2019). An increase of
N\textsubscript{2}O emissions is a usual trade-off. About 15\% of nitrogen inputs into the Po basin could be denitrified (Bartoli et al., 2012; Martinelli et al., 2018), however in some aquifers denitrification is lower than expected (Lasagna and De Luca, 2019). Ditches and canals and rice wetlands could boost denitrification if conservative management practices of in-stream vegetation are properly implemented (Soana et al., 2017; 2019). The problem of these curative solutions is that they could trigger N\textsubscript{2}O and therefore preventive measures at the farm scale are also recommended (Garnier et al., 2014). Some practices could indeed generate a process of pollution swapping. This is the case of practices that promote a reduction of green-house gas emissions while increasing leaching or the opposite, reducing leaching while increasing N\textsubscript{2}O emissions. An example is found in rice fields where dry seed can enhance leaching while clearly mitigate climate change (Miniotti et al., 2016)

Riparian buffers and buffer strips along agricultural fields in the alluvial plain of Po river were shown to remove nitrogen from groundwater, likely thanks to denitrification occurring in the first few meters of the buffer (Balestrini et al., 2011). Balestrini et al. (2011) looked at the efficiency of nitrogen removal in two riparian buffer strips located along irrigation ditches. The study site, in Bedollo and Linarola, is a typical flat agricultural area of the Po alluvial plain. The fields are drained by small channels dug every 33 m along the field and perpendicular to the ditch. Buffer strips were composed of mixed woody and herbaceous vegetation adjacent to fields of annual crops (wheat, maize, sugar beets). Crops were fertilized with combinations of manure and mineral fertilizers. Sampling of shallow groundwater wells showed steep gradients of nitrate loss from the fields to the irrigation ditches. For the Bedollo site the median nitrate concentration decreased from 29.2 mg NO\textsubscript{3}\textsuperscript{-}-N/L (south field) and 7.39 mg mg NO\textsubscript{3}\textsuperscript{-}-N /L (north field) to below detection level near the ditch. During rain events the nitrate concentration reached 91 mg NO\textsubscript{3}\textsuperscript{-}-N/L, and was reduced more than 90\% in the buffer. The sharp decreases in nitrate concentrations were likely due to denitrification occurring in the first few meters of the riparian buffer.

Balestrini et al. (2016) investigated the nitrogen buffering capacity of semi-natural riparian zones associated with spring-fed lowland streams (called fontanili). Fontanili areas are intensively cultivated and highly dependent on groundwater. The median nitrate concentrations in groundwater wells and springs ranged from 0.01 to 8.96 mg NO\textsubscript{3}\textsuperscript{-}-N/L, the nitrite concentrations from <0.005 to 0.134 mg NO\textsubscript{2}\textsuperscript{-}-N/L and the ammonium from <0.005 to 0.46 mg NH\textsubscript{4}\textsuperscript{+}-N/L. The maximum values, which were above the drinking water threshold, occurred when fertilization took place in winter and spring. The groundwater nitrate patterns in riparian areas were highly variable, with short nitrate plumes coming from adjacent cropland into riparian zones. Nitrogen removal efficiency varied from negligible to more than 90\%, depending on riparian zone characteristics like soil texture, organic carbon and hydraulic conductivity, riparian profile slope, and water table depth. Denitrification was the dominant nitrate removal mechanism, followed by physical processes (e.g. dilution).
Contamination of groundwater

Regarding nitrate, a large groundwater water quality database for the Po River was used by Cinnirella et al. (2005) to assess the spatial distribution of nitrate concentrations and its uncertainty. The data set consisted of mean annual nitrate concentration and standard deviation collected from 165 wells from 1986 to 1996. A significant increase in groundwater nitrate concentration, from 11.29 mg NO$_3^-$/L in 1986 to 27.03 mg NO$_3^-$/L in 1996 (with standard deviation of 8.82 to 16.12 mg NO$_3^-$/L respectively) is found. Using a probabilistic approach, the authors mapped areas of nitrate contamination and provided a model for assessing uncertainty of its spatial distribution.

In the western Po region, Lasagna et al. (2016) and Lasagna and De Luca (2019) studied groundwater-surface water (GW-SW) interactions and nitrate contamination. Lasagna et al. (2016) defined as “gaining streams” those where nitrate concentrations are higher in GW than in streams, and the nitrate concentrations in aquifers can be reduced by biological processes near the stream. The Po River and the Stura di Demonte River act as gaining streams in the Turin-Cuneo Plain. The nitrate profiles show the direct impact of agriculture on groundwater as well as the importance of the riparian areas in attenuating it. Nitrate concentration in groundwater progressively increase from the Alps to the plain due to accumulation of fertilizer excess. The shallow aquifer had high nitrate levels: 50% of monitored points had nitrate concentration between 25 and 50 mg NO$_3^-$/L, and 24% higher than 50 mg NO$_3^-$/L (up to 177 mg NO$_3^-$/L). Nitrate contamination varied with location and groundwater depth. The deep aquifer is more protected, and all water samples have nitrate levels below 50 mg NO$_3^-$/L. The most polluted areas are located in Poirino Plateau and in Cuneo plain, near the town of Fossano and Racconigi. Nitrate concentrations in the Poirino Plateau groundwater exceed 100 mg NO$_3^-$/L, and are up to 320 mg NO$_3^-$/L. Three general sources of nitrate contamination in shallow aquifer were identified (Lasagna and De Luca, 2019): manure, septic tank and a mixture of synthetic and organic sources. Hog and poultry manure were identified as the main source in the Poirino Plateau, cattle manure in Turin plain, and sewage under the city of Turin city.

Martinelli et al. (2018) assessed nitrate sources, concentrations, and processes in the groundwater of Northern Italy (Po and Veneto Plains). The aquifer system consists of shallow, unconfined aquifers and deeper, semi-confined and confined aquifers. High (greater than law limits) nitrate concentration were found in areas of high permeability, such as the alluvial fans of the Alpine and Apennine mountains, i.e. the recharge areas of the Po valley. High concentrations were related to either mineral fertilization or to organic matter sources. In contrast, the central and western plains had low nitrate concentration, which were attributed to denitrification processes. The authors could link areas of high nitrate concentration to mineral fertilizers, manure, septic systems, or mixed sources.

Pilla et al. (2006) used water chemistry and isotope geochemistry to assess the hydrodynamics of the Lomellina region, in south-west Lombardy. The region is drained by two Po tributaries,
Agogna River and Terdoppio River, and it is predominantly agricultural and industrial. The nitrate concentrations in two experimental wells ranged from 0.3 to 31.3 mg NO$_3$-L, with the highest nitrate concentration in the top 8-11 m and dropping significantly to below detection after that. The nitrate concentration in existing wells ranged from <1 (in 31 out of the 38 cases) to 23 mg NO$_3$-L. High concentrations (9.8 – 49.7 mg NO$_3$-L) were reported from springs, natural groundwater outflows, and very shallow wells. Ammonium concentrations of the experimental wells ranged from 0.03 to 0.1 mg NH$_4$+/L while those in the existing wells ranged from <0.05 to 0.77 mg NH$_4$+/L. Estimated radiometric age of the deep groundwater ranged from 251 to 11946 years. The study clearly shows the impact of agriculture to shallow aquifers as well as the importance of protecting deep groundwater.

Sacchi et al. (2013) focused on the Lombardy plain of the Oglio and the Lambro rivers, two major Po tributaries. There are two plain areas, the higher plain with significant infiltration, and the less permeable lower plain, separated by a “spring belt”. The groundwater system comprises four aquifers, the top one is unconfined, the second is semi-confined, and the two deeper ones are confined. The authors reported the nitrate concentration of the top aquifers from 2001 to 2010. The highest concentrations of nitrate, up to 180.2 mg NO$_3$-L, were seen in the top aquifer where 9% of the monitored wells had nitrate levels above the drinking water standards of 50 mg NO$_3$-L. The second aquifer had the highest long-term mean nitrate concentration, ranging from 21.1 to 29.1 mg NO$_3$-L, with 6% of wells above drinking threshold aquifer. Nitrates were lower in the third aquifer, below drinking threshold at all monitoring points. The lower plain had concentrations less than 25 mg NO$_3$-L. In terms of sources, N load inputs ranged from 110 to 197 kg N/ha/y of mineral fertilizers, from 32 to 179 kg N/ha/y of manure, from 11 to 76 kg N/ha/y of industrial emissions, and from 8 to 56 kg N/ha/y of urban sources. The total accumulation of nitrate in the groundwater was estimated at about 1 t NO$_3$-N/ha, 80% of which on average came from agriculture.

Several works focused on the nitrogen balance and fate in the Oglio River watershed and the role of groundwater, with sampling campaigns that comprised the main watercourse, tributaries, pollution sources, springs, and groundwater (Soana et al. 2011; Bartoli et al., 2012; Deloconte et al. 2014; Rotiroti et al., 2019). About 60% of the Oglio River watershed is arable land, and maize is the dominant crop covering about 65% of the arable surface. Traditional agronomical practices have profoundly modified the surface–groundwater equilibrium and chemical characteristics of the freshwater system. The area has significant livestock population. The amount of manure produced is 3 times higher than what could be spread in the watershed. The large agricultural nitrogen surplus generates nitrogen saturation in the soil and high nitrogen concentrations in all water compartments of watershed. Soana et al. (2011) estimated a total of 100,115 t N/y input to the lower Oglio River basin (51% from livestock manure, 33.5% from mineral fertilizers, 12.1% from biological fixation, and the rest from atmospheric deposition and sewage sludge) and 60,060 t/y output from the basin (65% crop uptake, 21% ammonia volatilization and the remaining denitrification from soils). The mean weighted surplus was
estimated to about 180 kg N/ha/y. The watershed exported about 60 kg N/ha/y (33% of the surplus), with the remaining stored or reacting in the groundwater. The groundwater nitrate concentrations ranged from below detection to 16 mg NO₃⁻-N/L in the higher plain (average 6 mg NO₃⁻-N/L), and from below detection to 12 mg NO₃⁻-N/L in the lower plain. The mean nitrate concentrations of the top aquifer of the lower Oglio river ranged from less than 1.2 to 19.3 mg NO₃⁻-N/L (2002-2008 data). According to Bartoli et al. (2012) livestock manure and mineral fertilizers contribute 85% of total nitrogen inputs (about 100,000 t N/yr). Nitrogen crop uptake, soil denitrification and volatilization were estimated at about 60,000 t N/yr. Denitrification in the Oglio riverbed and riverine wetlands could account for a further 20% nitrogen removal.

In the upstream reaches during the irrigation period, up to 90% of the natural river flow is diverted for irrigation and industrial purposes. The irrigation water excess leaches down nitrate, which is subsequently denitrified; when groundwater returns to the Oglio River, it modifies the river water composition in the downstream reaches. A map of nitrate-N concentration in the shallow aquifer showed values of 4-7.2 mg NO₃⁻-N/L (Bartoli et al., 2012); nitrate concentration collected from springs ranged from 30 to 50 mg NO₃⁻-N/L while the groundwater well data had nitrate concentrations around 18 mg NO₃⁻-N/L (Deloconte et al., 2014). Rotiroti et al. (2019) assessed the effects of irrigation on groundwater. Data were collected from groundwater, rivers and springs along about 95 km of the Oglio River extending from Lake Iseo to the confluence with Mella River. In the higher plain, nitrate concentrations in many aquifers exceeded the regulatory limit of 50 mg NO₃⁻/L (D. Lgs. 30/09, 2009). Spring water reflected the composition of groundwater in the higher plain aquifer. Nitrate concentrations were higher in groundwater and springs in the higher plain (median of 39.8 and 40.6 mg NO₃⁻/L, respectively) than in the lower plain, where concentrations were generally below detection. The study also showed that irrigation during the summer months increases the water table level up to 4 m and dilutes nitrates, with a beneficial effect on the high plain aquifer. Available data thus suggest that in the central part of the watershed groundwater accumulates nitrogen, which is then being discharged via springs to surface water. In the middle reach, groundwater inputs are responsible for a tenfold increase of nitrate in river water (from 2.2–4.4 up to 33.5 mg NO₃⁻/L). This is more evident in summer, when discharge is lower. These studies indicate that reducing nitrate delivery to the Adriatic Sea would require addressing groundwater contamination, with expected long recovery times.

The study site of Rapti-Caputo and Martinelli (2009) was the central sector of the Ferrara Plain. The objectives of the study were to determine the recharge area of the groundwater, understand the mixing between the unconfined and confined aquifers, and evaluate the mean residence time of groundwater. The nitrate concentrations in the unconfined aquifer ranged from 6 to 152 mg NO₃⁻/L with a mean of 65 mg NO₃⁻/L, and for the confined aquifer ranged from 0.4 to 3.2 with a mean of 1.6 mg NO₃⁻/L. The isotopic composition of the confined aquifer showed a slow mixing regime with the Po river and direct infiltration of precipitation (water originating from the Alps and from the Apennines). The mean residence time was estimated at
2-5 years. This study illustrated not only the impact of agriculture to the shallow, unconfined aquifer, but also the vulnerability of the deep, confined aquifer.

Mastrocicco et al. (2017) assessed the origin and fate of nitrogen and chlorate in the shallow unconfined aquifer of Ferrara province, in the Po delta. Perchlorate is an impurity in many fertilizers and its by-products (chlorate and chlorite) in groundwater can indicate agricultural contamination. Nitrate concentrations ranged between below detection to a maximum of 456 mg NO$_3^-$/L, with a mean value of 6.8 mg NO$_3^-$/L, with higher values found for sandy soils and oxic environments, and lower for peat soils. Nitrate is suggested to be due to agricultural sources. Ammonium concentrations ranged from 0.01 to 68 mg NH$_4^+$/L with a mean value of 6.3 mg NH$_4^+$/L. The origin of ammonium is the mineralization of CO(NH$_2$)$_2$, urine as well as mineral fertilizers. The highest values of ammonium were found in peat soils.

Nitrite concentrations were quite low ranging between 0.01 to 15.3 mg NO$_2^-$/L with an average value of 0.3 mg NO$_2^-$/L. The origin of nitrite is denitrification of nitrate, another intermediate of denitrification, before reduction to N$_2$O and N$_2$. Chlorate presence was detected in June sampling in 49 out of the 56 wells, with mean concentration of 2.9 mg ClO$_3^-$/L (range: 0.01 to 38.1 mg ClO$_3^-$/L). The highest maximum concentration was recorded in loam soils (38.13 mg ClO$_3^-$/L), followed by sandy soils (21.57 mg ClO$_3^-$/L), whereas clay and peat soils has lower maximum values (1.239 and 0.507 mg ClO$_3^-$/L respectively).

Concerning contamination of herbicides, in 2009, more than 40 lowland springs in the central area of the Po river plain were sampled for nitrate and commonly used herbicides, namely desethylterbuthylazine (DET), terbuthylazine (TBA), acetochlor, alachlor, isoxaflutole and aclonifen (Laini et al. 2012). The mean nitrate concentration at the springs was 8.48 ± 4.89 mg NO$_3^-$-N/L. Terbutylazine (TBA) and its metabolite desethylterbuthylazine (DET) were detected at concentrations up to 197 ng/L for TBA and 388 ng/L for DET in Lombardy. These herbicides are likely coming from annual crops cultivated nearby the springs. Conversely, in springs of Emilia-Romagna no herbicide was detected, probably due to absence of maize cultivation. In total, 16 out of the 84 analyses resulted in herbicide concentrations higher than the drinking water standard (100 ng/L). The persistence of herbicides was considered low, and the authors recommended that measures to avoid contamination should focus on management of fields adjacent to the springs (0-1800 m), and should concern optimization of irrigation practices, restoration of buffer strips, and crop rotation.

Impact on coastal areas
The North Adriatic Bay suffers episodic eutrophication crisis (Cozzi and Giani, 2011). Eutrophication takes various forms with development of harmful algal blooms (HAB), with accumulation of mucilaginous algae or dinoflagellates leading to hypoxia and producing toxic substances.
Eutrophication potential is linked to the excess of nutrients delivery over that of silica (an element that favors diatoms) to a coastal bay system. This excess can be quantified with the indicator for coastal eutrophication potential ICEP (Billen and Garnier, 2007, on the basis of the nutrient ratios by Redfield et al., 1963 and Conley et al., 1989). An ICEP value close to zero indicates equilibrium between nitrogen or phosphorus and silica, whereas positive values mean an excess of nutrients with respect to silica, i.e. a potential for coastal eutrophication. In the Po coastal zone, the ICEP-N value is currently estimated at 15.5 and ICEP-P at -0.12 kg C/km²/d. Thus, while a relative balance has been reached between phosphorus and silica, nitrogen excess is still large and potentially conducing to eutrophication.

In conclusion, research highlighted the severe impact of agriculture to freshwater and coastal zones in the Po River Basin. Excessive fertilization and manure spreading are major sources of nitrogen surplus, which leaches into aquifers, particularly the shallow, unconfined one. From these underground sources, nitrates may exchange with surface waters and affect springs and rivers. The lower confined aquifers have less contamination, but they are still vulnerable to agricultural impacts. Better nutrient management, riparian strips and buffers are areas of active denitrification and can be used to mitigate agricultural pollution. Overall, the Po basin aquifers have been significantly impacted by agriculture and any remedial measures will take long time to show results.
References


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