UNIVERSITÀ DEGLI STUDI DI PADOVA

DIPARTIMENTO DI INGEGNERIA INDUSTRIALE

CORSO DI LAUREA MAGISTRALE IN INGEGNERIA CHIMICA E DEI PROCESSI INDUSTRIALI

Tesi di Laurea Magistrale in
Ingegneria Chimica e dei Processi Industriali

Optimization of the carbon capture and sequestration supply chain for the Italian cement industry

Relatore: Prof. Fabrizio Bezzo

Correlatore: Dott. Federico d'Amore

Laureando: STEFANO CROSATO

ANNO ACCADEMICO 2019-2020

Abstract

The development of the industrial activities of our modern civilization have greatly increased the greenhouses gases emission causing the global warming to be a more concerning issue. With the increased urbanisation, concrete production is becoming more important since it is the second most used commodity after water, but one of his constituents, cement, is responsible of 5% of the global manmade carbon dioxide emissions. Carbon capture and sequestration technologies are currently the only viable route to reduce emissions.

In this thesis a mixed integer linear programming model is proposed, with the aim of optimising an Italian supply chain for carbon capture and sequestration of carbon dioxide emissions from the cement industry. The key parameters of the model are the efficiencies and costs of the capture technologies considered, the suitable geological sequestration basins, both onshore and offshore, and the techno-economic data of the transport infrastructure. A k-means methodology is implemented to represent the possibility of merging carbon flowrates from cement plant and determine larger-scale collection clusters. Then, the outputs of the model, are the final net carbon dioxide emissions after capture and the costs to install and operate the entire supply chain, these subdivided into capture, transport and sequestration costs shares. The model is optimised for different objective functions, aiming at the minimisation of costs (economic objective), at the minimisation of net overall emissions (environmental objective), or a combination of both (bi-objective optimisation).

The best economic networks entail the installation of only one capture technology, i.e. calcium looping with a total cost of 8.53 B€ (64.5 €/t) for a carbon reduction of 50%. Oppositely, the environmental optimisations can reach a reduction of 81% with a total cost of 14.7 B€ (67.8 €/t).

Riassunto esteso

Il progressivo sviluppo industriale ha portato a un aumento considerevole dei cosiddetti gas ad effetto serra con conseguente peggioramento del riscaldamento globale. Ciò ha portato alla ricerca di una soluzione per ridurre le emissioni globali di inquinanti. In particolare, in Europa, uno degli obiettivi chiave che si vuole raggiungere prima del 2030 è la riduzione del 40% delle emissioni rispetto ai livelli del 1990. I gas che contribuiscono all'effetto serra sono: il diossido di carbonio, gli ossidi di azoto, metano e i clorofluorocarburi. Tra questi, il diossido di carbonio costituisce circa l'81% delle emissioni globali ed è fondamentale abbatterle. A fronte di questa necessità, l'utilizzo della cattura e sequestro del carbonio è una delle soluzioni con più aspettative per raggiungere questo obiettivo, grazie al fatto che la sua implementazione non richiederebbe modifiche al settore energetico ed industriale.

Il cemento è uno dei materiali più usati al mondo in diversi ambiti, secondo solo dopo l'acqua, e l'avanzamento dell'urbanizzazione richiederà quantità sempre più elevate con gli anni a venire. Tuttavia, le emissioni di CO_2 legate alla produzione del cemento costituiscono circa il 5% delle emissioni globali antropiche, e purtroppo non è possibile ridurre in modo significativo l'emissione solo con sistemi di ottimizzazione dell'efficienza del processo o utilizzando combustibili a basso contenuto di carbonio fossile. Per questo motivo, la cattura e il sequestro della CO_2 assume più valore come soluzione. Tuttavia, se lo studio della sua applicazione sull'industria energetica è stato portato avanti negli anni ottenendo notevoli risultati, per quanto riguarda l'industria del cemento ci sono ancora delle incognite.

L'obiettivo di questa tesi magistrale è proporre un modello matematico in grado di realizzare una filiera produttiva per la cattura e il sequestro della CO_2 adattato al panorama italiano dell'industria del cemento. Il modello si concentrerà sull'effettivo abbattimento delle emissioni di CO_2 e sui costi di installazione e operazione divisi in tre gruppi: la cattura, il trasporto e il sequestro. Per la cattura, la caratteristica fondamentale è la scelta di una tecnologia di cattura, di cui sono disponibili tre opzioni di post-combustione considerate per questo lavoro. Per il trasporto, il panorama italiano è stato analizzato per tre diversi tipi di clusterizzazione per studiare l'infrastruttura ottimale della catena di filiera. Infine, il sequestro è diviso tra onshore e offshore, in base alla posizione del bacino

geologico ritenuto adatto al sequestro. Con questi input il modello è stato formulato come un problema di programmazione lineare a variabile miste lineari e intere.

Sono state implementate tre tipi di ottimizzazione del modello. La prima è quella economica, che vuole ridurre al minimo i costi avendo come condizione l'abbattimento di una percentuale minima delle emissioni iniziali. La seconda è quella ambientale, in cui l'obiettivo è ridurre al minimo le emissioni di CO_2. Infine, un'ottimizzazione multi-obiettivo è stata eseguita per studiare i conflitti che possono esserci tra i due casi precedenti e trovare il compromesso migliore. Queste ottimizzazioni sono state eseguite considerando due tipi di scenario diversi in cui l'intensità di carbonio, usata per calcolare le emissioni aggiuntive dovute all'utilizzo della tecnologia di cattura, varia. Per il primo scenario si considera il mix energetico italiano, mentre per il secondo si considera di utilizzare energie rinnovabili per i sistemi di cattura.

Dalle ottimizzazioni economiche ed ambientali nello scenario che utilizza il mix energetico italiano è risultato che una delle tre tecnologie di cattura, il calcium looping, è sempre selezionata in ogni caso. Inoltre, la massima riduzione di carbonio ottenibile per il caso ambientale è dell'81%, e il sequestro è sempre onshore per minimizzare non solo i costi ma anche le emissioni dovute al trasporto. Poiché la stessa tecnologia viene considerata in entrambi i casi, il multi-obiettivo non ha mostrato nessun conflitto tra le due ottimizzazioni, ma bensì, una relazione lineare tra i due. Dai casi analizzati, usando otto clusters, si ottiene sempre la migliore ottimizzazione per la parte del trasporto. In media, per un abbattimento del 50% delle emissioni iniziali, il costo è di 64.5 €/t. Nello scenario delle fonti rinnovabili, il calcium looping è sempre selezionato per l'ottimizzazione economica, ma per quella ambientale, la tecnologia a membrane predomina abbattendo le emissioni fino al 90% ma con un costo specifico di 99.1 €/t. Per questa differenza, il multi-obiettivo ha mostrato un conflitto tra i due ottimi, ed è risultato che è possibile avere una configurazione intermedia in cui il calcium looping è sempre scelta per la maggioranza dei nodi, però, viene impiegata per alcuni la tecnologia a membrane. Questo permette di raggiungere una riduzione totale dell'85% con costo specifico di 69.3 €/t.

Index

List of Figures

List of Tables

List of symbols

Acronym

AITEC	= Associazione Italiana Tecnico Economica del Cemento
CaL	= Calcium Looping
CAP	= Chilled Ammonia Process
CCS	= Carbon capture and sequestration
ECO	= Economic optimisation of the model
EEA	= European Environmental Agency
ENV	= Environmental optimisation of the model
E-PRTR	= European Pollutant Release and Transfer Register
GAMS	= General Algebraic Modelling System
GHG	= Greenhouse Gas
IPCC	= International Panel on Climate Change
ISPRA	= Istituto superiore per la protezione e la ricerca ambientale
MAL	= Membrane-Assisted Liquefaction
MILP	= Mixed Integer Linear Programming
MULTI	= Multi-objective optimisation of the model
SC	= Supply Chain

Sets

c	{c1,…, cX, c101,…, c114}	Centroids of the subcase considered, and the sequestration nodes included in the model
$cluster^C$	{c1,…, cX}	Subset of only centroids
k	{k1, k2, k3}	Capture technologies: CAP, MAL and CaL
n	{1,…,29,101,…,114}	Capture and sequestration nodes
o	{CO_2, cost}	E and TC functions for MULTI case
$o1_o$	{CO_2}	First element of set o
$om1_o$	{cost}	Second element of set o
p	{p1, p2, p3, p4}	Discrete flowrates
$seque^C$	{c101,…, c114}	Subset of only sequestration nodes
$seque^N$	{n101,…,n114}	Subset of only sequestration nodes
t	{1,…,20}	Time interval in years

Scalars

α	= X (fixed value based on the case)	Carbon target reduction [%]
E^{pump}	= 5.91	Specific emissions for the transport [gCO_2/t/km]
R	= 6732.785	Radius of the Earth [km]
selOBJ	= {0;1} (based on case)	Selection of the single objective function
USC	= 7.20	Unitary sequestration cost [€/t]

Parameters

$\Delta E_{k,t}^{el}$		
$\Delta E_{k,t}^{coal}$	[t of CO_2 released/ t of CO_2 captured]	Indirect emission of technology k due to the sources used
$\Delta E_{k,t}^{gas}$		
E_t^0	[t of CO_2]	Initial emission at time t
$F_{c,cp}$		To determine an onshore or offshore transport
$LD_{x,y}$	[km]	Linear distance between point x and y
η_k	[%]	Efficiency of technology k
$NC_{n,c}$		To identify which n belongs to which c
off_c		To determine an onshore or offshore sequestration
UCC_k	[€/tCO_2]	Unitary Capture Cost for technology k
UTC_p^{on}	[€/km]	Unitary Transport Cost onshore of flowrate p
UTC_p^{off}	[€/km]	Unitary Transport Cost offshore of flowrate p
$z_{n,p}$		To determine the flowrate p from a capture node

Variables

ΔE	[t of CO_2]	Total additional direct and indirect emission
E	[t of CO_2]	Final net CO_2 emission
E^{out}	[t of CO_2]	Final sequestrated CO_2 emission
$E^{pump,tot}$	[t of CO_2]	Final transport CO_2 emission
$E_{k,n,t}^{in,CAPT}$	[t of CO_2]	Captured CO_2 amount in node n, at time t, with technology k
$E_{c,t}^{in}$	[t of CO_2]	Total CO_2 captured in cluster c at time t
$E_{c,t}^{out}$	[t of CO_2]	Total CO_2 sequestrated in cluster c at time t
$E_t^{C,pump}$	[t of CO_2]	Additional inter-transport CO_2 emission
$E_t^{N,pump}$	[t of CO_2]	Additional intra-transport CO_2 emissions
E_t^{out}	[t of CO_2]	Total CO_2 sequestrated at time t
$Q_{p,n,c,t}^{N}$	[t of CO_2]	Intra connection flowrate
$Q_{p,c,cp,t}^{C}$	[t of CO_2]	Inter connection flowrate
TC	[B€]	Total cost
TCC	[B€]	Total Capture cost
TSC	[B€]	Total sequestration cost
TTC	[B€]	Total transport cost

Discrete variables

$\gamma_{k,n}$	{0;1}	0 capture technology k not selected for node n; 1 capture technology k selected for node n
$\lambda_{p,c,cp,t}^{C}$	{0;1}	0 no transport between c and cp, 1 transport between c and cp at time t with flowrate p

Introduction

The threats related to the global warming brought 195 countries to sign the Paris Agreement in 2015, during the XXI Conference of the Parties of the United Nations Climate Change Conference. The aim is to strengthen the global response to the issues caused by the climate change by keeping a global temperature rise of this century below 2°C compared to pre-industrial levels, and preferably to push in limiting the increase even further 1.5 °C before 2050 (UNFCC, 2015). To achieve this objective, the greenhouse gas (GHG) manmade emissions must decrease. Carbon dioxide share of these GHG is about 81% (EPA, 2018), and 5% of all the manmade CO_2 emissions are from the production of concrete. Concrete is a nowadays the second most used commodity after water (CEMCAP, 2018) and with the increasing urbanisation more and bigger volumes of concrete will be required which will cause an increase in the CO_2 emissions. The biggest issue regarding the concrete, or to be specific, in the cement production process, it is impossible to avoid or greatly decrease the emissions through energy optimization and the use of renewable fuel (CEMCAP, 2018). Because of this, the only viable solution to abate the CO_2 emission respecting the Paris Agreement is the employment of a carbon capture and sequestration (CCS) technology. However, around the world only 48 CCS plant were operative in 2018 (Global CCS Institute, 2017), and for the cement industry the capture technologies did not have a technology readiness level high enough for a commercial use in 2015 (Hills et all, 2015). CEMCAP in the time period from 2015 to 2018 studied and upgraded the capture technology till a TRL 6 at least to prepare the ground for a large-scale introduction to CCS in the European cement industry (CEMCAP,2018). In view of this objective, this Master Thesis aims to propose a mathematical model for an initial quantification of the costs and the possible CO_2 reduction on the Italian cement industry. The key parameters will be the capture technologies performances after the upgrade by CEMCAP studies, the geological basins for the sequestration of the capture CO_2 that can be onshore or offshore and the transport infrastructure. For this stage, a k-means clustering methodology is implemented to represent the possibility of merging carbon flowrates from cement plant and determine larger-scale collection clusters. The model, with these inputs, will be written as a mixed integer linear programming problem and optimise to achieve the minimum total cost for installation and operation of the CCS

supply chain (SC) while achieving a set carbon reduction target, or the minimum final net CO_2 emission after capture. A multi-objective study will be carried out too to analyse the possible conflicts of the two optimums to find the best compromises, if it exists.
The structure of this Master Thesis is as follow:

- Chapter 1 describes the global warming, the reason because GHG must be decreased and the CCS as possible solution to it analysing it passing from a global view to the Italian cement industry.
- Chapter 2 provides a description of the cement production process, and of the possible capture technologies to implement for a CCS SC, analysing the additional emissions and costs of them.
- Chapter 3 describes the mathematical model of the CCS SC; the assumptions done, what parameters are taken into consideration, how the inputs data are rearranged, and what will be the case studies.
- Chapter 4 is about the comment and discussion of the results obtained from the different optimisations done of the model. Firstly the single objective economic optimisation are presented, then the environmental ones and lastly the multi-objective results.
- Conclusions and final remarks

Chapter 1

CCS as possible solution for the CO_2 reduction

This chapter is just an overview on the climate change and its consequences, explaining the role that the CCS can have in reducing CO_2 emissions on a global level and why it must be applied to the cement industry.

1.1 Global warming

With the progressive development of the industrial activities, the greenhouse gasses (GHG) emissions greatly increase. GHG are constituted by carbon dioxide, methane, nitrous oxide and chlorofluorocarbons and other gases. In 1990 GHG emissions grew from 10.37 $GtCO_2eq$ to 15.44 $GtCO_2eq$ in 2010 (IPCC,2014). This increment is mainly driven by three factors: population growth, economic growth and the loss in efficiency for the natural environment to absorb, reflect and emit CO_2 (IPCC, 2014).

Usually an economic growth implies a population growth and there will be the need to satisfy the increasing energy demand, which, today, 80% of the global primary energy is produced by burning fossil fuels and this correspond as a consequence to a in increase in GHG emissions (BP, 2018; IEA, 2016). Moreover, the CO_2 ,which its share is 81% of all the GHG emission (EPA, 2018), is raising by 1.3% every year from the data obtained between 2006 and 2016 (BP, 2016). This can be explained by the contribution of China, India and other countries of Asia, which are still experiencing a growth in the population and in the energy demand (IEA,2016).

Because of this excessive increase in the amount of manmade GHGs, the climate is changing with dangerous effects for the environment and human. The most notable effect on environmental are on glacier that have shrunk, ice on rivers and lakes is breaking up earlier, plant and animal ranges have shifted, and trees are flowering sooner. Taken as a whole, the range of published evidence indicates that the costs of climate change will greatly increase over time and to be significant (IPPC, 2013). The atmospheric concentration of CO_2 has increased from 280 ppm to 440 ppm between 1860 and now; this caused the increment of the average surface temperature of about 0.85°C between 1880 and 2012 (IPCC, 2018). This CO_2 concentration is responsible for 26% of the acidification of the oceans, equivalent to a decrease of 0.1 in the pH, which increase the seal level of 0.19 m from the measurement in 1979 (IPCC,2014). Without any actions to prevent the increase of the GHG emissions, the temperature on Earth is expected to increase from 1.9 to 3.4 °C with respect to pre-industrial level by 2100 that would be bring disastrous consequence on the life of billions of people (IPCC, 2018).

1.2 CCS as possible solution

If no action is taken in trying to decrease effectively the GHG in the atmosphere the effects of the global warming could harm the environment and the people. In the last decades, already in 1998, global warming raised some concern as consequence of the increase of GHGs, that brought to the foundation of The Intergovernmental Panel on Climate Change (IPCC), but only with Kyoto Protocol the first measures to reduce GHG emissions were adopted. In 2015, with the Paris Agreement, 195 nations agree in trying to avoid the temperature raise over 2 °C with the respect to pre-industrial level, and preferably limiting the rise to 1.5°C by 2050 (UNFCCC, 2015).
One of the few technologies that can avoid the direct emission of CO_2 in the atmosphere and helping then in this fight against the climate change is the carbon capture and sequestration (CCS). CCS operates in a way to remove large quantities of CO_2 generated from power plants or industries, subtracting it with a chemical or physical process (i.e., absorption process through ammine; membrane process), and sequestrating the CO_2 in suitable geological basins (IPCC, 2005).

The first step is the capture. It consists in separating the CO_2 from a stream through a chemical or physical process to concentrate the CO_2 . The concentrated CO_2 stream will be purified, if necessary, and then compressed to be transported without excessive costs. The second step is the transport that can be via pipeline or even using ships toward the sequestration site (IPCC, 2005). The third step consists in injecting the CO_2 underground in a supercritical state. Otherwise it could be re-utilized in other processes, but until now, there are no process that requires such volumes, making this alternative quite limited.

At the beginning, CCS was employed mostly in the energy sector, since it is from there the highest CO_2 emission. In particular, five areas were identified as main responsible for GHG emissions: power generation, residential building and tertiary, manufacturing industries and construction, transport and others (IPCC, 2018). Because of this, the study of CCS on other sectors is not developed as much as the one on the energy sector. However, in the last years, CCS importance was recognized more and more, and the European Community funded different research projects (Horizon 2020, NER 300, Life climate action, etc.) to develop or optimize technologies to decrease the GHG emission. From one of these projects, CEMCAP born, in regarding to prepare the ground for a large-scale implementation of CCS into the cement industry (CEMCAP, 2018). In fact, the production of cement is responsible for 5% of the global CO_2 manmade emission (CEMCAP, 2018), and the only viable solution to abate the CO_2 is using a CCS technology. It is the only solution because, it is not possible to significantly decrease the emissions, since it is an inherent characteristic of the production process.

Chapter 2

Cement process and capture options

In this chapter the cement production process will be explained with the possible capture technologies that can be applied to the cement plant.

2.1 Cement production process

It is necessary to understand the cement production process and why the only viable way to decrease the CO_2 is employing CCS technology. From the Technology Roadmap: Low-Carbon Transition in the Cement Industry (2009), the process is divided into three stages: raw material preparation, clinker production and clinker grinding that is a mix with other components to produce cement. The cement manufacturing can be explained in ten steps:

1. Quarrying raw materials. It consists in extracting from natural calcareous deposits the key ingredients for cement like limestone.
2. Crushing. The material extracted are then crushed with a size below 10 centimetres
3. Preparing raw materials. A chemical process called “prehomogenisation” is carried out by mixing the materials, which will be milled into a fine powder called raw meal.
4. Preheating and co-processing. The raw meal is heated through a counter current mixing with the hot kiln exhausted gases to reach a temperature over 900°C.
5. Precalcining. It is the decomposition of limestone into lime in a combustion chamber which is partly in the kiln. The 60-70% of CO_2 emissions is released from this chemical process. The rest is generated by the fuel combustion, which burn nearly 65% in this step

6. Producing clinker in the rotary kiln. The precalcined material is then sent into the kiln where temperature is up to 1450 °C. The intense heating partially melts the meal into clinker. In this step, the calcination of the limestone is completed and there are the last CO_2 emissions.
7. Cooling and storing. The hot clinker is then cooled rapidly to 100 °C through the use of air blowers.
8. Blending. It is the mix of the clinker with other material to give the cements specific mechanical and physical properties.
9. Grinding. Lastly, the final mixture is ground to a grey powder, called Portland cement (PC).
10. Storage. The product is homogenised and then stored for dispatch.

In step 5, the chemical decomposition can be described through Eq. (2.1), and until lime is used as base material for the clinker, it is not possible to avoid it.

$$CaCO_3 \xrightarrow{900\,^{\circ}C} CaO + CO_2 \tag{2.1}$$

From 1 mole of limestone (calcium carbonate), 1 mole of lime (calcium oxide) and 1 mole of carbon dioxide are obtained, which is equivalent to nearly 880 kgCO_2 per tonne of clinker (MacDowell, et al., 2010). This means that an energy optimization and even the use of renewable fuels can only partly reduce the CO_2 emission (CEMCAP, 2018). Therefore this confirms that alternative options must be considered for the CO_2 abatement, and one of the most promising options is the carbon capture and sequestration.

2.2 Capture technologies

Many capture technologies are available and generally compatible with CCS activity, but only few managed to be accepted from an industrial point of view (MacDowell, et al., 2010). In general, three technologies are considered suitable for commercial use: amine solvents, oxyfuel and calcium looping. However, most, if not all of them were employed in the energy industry and not for the cement industry. In fact, for the cement industry, the technology readiness level (TRL) was from level 4 to level 6 at best in 2015 (Hills, et al., 2015). A TRL of 6 is reached when there is a demonstration of the technology using a pilot-scale prototype in a relevant environment, meaning

that all the technology below TRL 6 are still tested and studied on a laboratory scale environment. One of the projects funded from the European Union's Horizon 2020 research and innovation program is CEMCAP (CEMCAP, 2018). In 2015, CEMCAP project started and its objective was to prepare the ground for large-scale implementation of CO_2 capture in the European cement industry. (CEMCAP, About, 2018). For reaching this objective, CEMCAP studied and developed the oxyfuel technology and three fundamentally different post combustion capture technologies to TRL 6 at least, fixing a capture rate of 90%. In this model, the three post-combustion capture technologies will be considered as capture options. The descriptions are based on the article Comparison of Technologies for CO_2 Capture from Cement Production – Part 1: Technical evaluation (Voldsund, et al., 2019).

1. The chilled ammonia process (CAP). It is a post-combustion technology using the chilled ammonia as solvent to absorb and then remove from the flue gases the CO_2. The retrofit is simple, with minor modifications required for heat integration. The exhaust passes through a cold ammonia-water mixture which absorb CO_2, which is then separated adding heat to the solution in a subsequent vessel to be purify and pressurized for transport. The ammonia can be recovered and recycled into process. This process requires a heat generator to regenerate the solvent and recover the ammonia.
2. Membrane – Assisted CO_2 Liquefaction (MAL). It can be retrofitted without any modification to the cement plant. Through the use of a polymeric membrane it is possible to increase the flue gas CO_2 concentration which will be separated through a liquefaction process. The pressure difference and ratio over the membrane module is generated both by the flue gas compression on the feed side and vacuum pumps on the permeate side of the membrane. The efficiency and chemical stability of the membrane depends on the type of polymer and the tolerance to SO_x and NO_x. Only electric power is required as input to the process.
3. Calcium Looping – Tail End Configuration (CaL). It is based on the reversible carbonation reaction ($CaO + CO_2 \leftrightarrow CaCO_3$) exploited to remove the carbon dioxide from flue gas. It is possible to implement the technology without any modification to the plant. The flue gas is sent to a carbonator where CO_2 is removed by a reaction with a calcium oxide-based sorbent. This sorbent can be regenerated when coal is burnt under oxyfuel conditions to

reach the calcination temperature of 920 °C in a calciner. The captured CO_2 will undergo a purifying treatment before being transported. An additional supply of limestone and coal is needed for this process.

In these three technologies, the equipment requires energy from different sources to operate. However, consuming electric power, or burning natural gas in a heater, or supplying more limestone and coal to the cement plant, will cause an additional emission of CO_2 which can be direct or indirect based on the type of equipment. Therefore it is necessary to calculate how much CO_2 is generated by each technology per 1 tonne of CO_2 captured to find parameters that have a general validity and can be applied to the model.

2.2.1 Efficiencies, additional emissions and costs

In Section it will be explained how the additional emissions related to a capture technology are calculated.

First of all, ΔE_k^i is defined as the amount of CO_2 released per amount of CO_2 captured, Eq. (2.2).

$$\Delta E_k^i = \left[\frac{\text{t CO}_2\text{emitted}}{\text{t CO}_2\text{ captured}}\right] \tag{2.2}$$

There are two ways to calculate this parameter. One is by having the amount of CO_2 emitted $E_{CO_2}^i$ [$\text{tCO}_2\text{emitted}$] due to the additional energy consumption and then the amount of CO_2 captured $E_k^{in,capt}$ [tCO_2 captured] from technology k, as described in Eq. (2.3)

$$\Delta E_k^i = \frac{E_{CO_2}^i}{E_k^{in,capt}} = \left[\frac{\text{t CO}_2\text{ emitted}}{\text{t CO}_2\text{ captured}}\right] \tag{2.3}$$

The other way is by having the specific emission of CO_2 related to the energy consumption of the additional fuel $e_{CO_2}^i$ [t CO_2 emitted/MJ], with the total amount of energy U^i [MJ] consumed and $E_k^{in,capt}$ [t CO_2 captured] as in Eq. (2.4).

$$\Delta E_k^i = e_{CO_2}^i \cdot \frac{U^i}{E_k^{in,capt}} = \left[\frac{\text{t } CO_2 \text{ emitted}}{\text{MJ}}\right] \cdot \left[\frac{\text{MJ consumed}}{\text{t } CO_2 \text{ captured}}\right] \quad (2.4)$$

The additional emissions are divided on the base of the additional fuel considered. When it is electricity the additional emissions are indirect, while when natural gas or coal are burnt, those are direct emissions. Regarding the indirect emissions, the carbon intensity of the energy mix used must be know and it will be equal to $e_{CO_2}^i$. Therefore, from the annual report of Istituto Superiore per la Protezione e la Ricerca Ambientale (ISPRA, 2018), three different energy mix are reported with their carbon intensity, and from the European Enviroment Agency the carbon intensity of the Italian energy mix is found (EEA,2018).

1. Renewable sources: 0.0 [gCO_2/kWh]
2. Italian electricity mix: 256.2 [gCO_2/kWh]
3. Natural Gas Combined Cycle Plants: 389.1 [gCO_2/kWh]
4. From coal plants: 897.6 [gCO_2/kWh]

When using renewable energies the carbon intensity is equal to 0, because the emission of CO_2 is considered part of the natural carbon cycle and not part of the man-made emissions that must be decreased.

From the review of Voldsund et al., (2019) all the necessary data are retrieved and reported in Table 2.1. With these data is possible to calculate with one of the two equations the additional emissions, however, some considerations must be done for the CaL technology and the carbon capture ratio (CCR) reported.

Table 2.1 – Specific emissions [kg/ton_{clk}], efficiencies [%], energy consumptions [MJ/ton_{clk}] and clinker production (t_{clk}/h) of the reference cement plants and the post-combustion capture technologies. (Voldsund, et al., 2019)

	VDZ ref.	PoliMi ref.	CAP	MAL	CaL
Direct CO_2 emissions at stack (kg/ton_{clk})	846	865	83	84	78
Direct CO_2 emissions due to steam generation (kg/ton_{clk})	0	0	104	0	0
Indirect CO_2 emissions (kg/ton_{clk})	34	34	53	109	15
CO_2 capture ratio (CCR) (%)	-	-	90	90	94
CO_2 avoided from flue gas (AC_{fg}) (%)	-	-	90	90	91
Equivalent CO_2 avoided (AC_{eq}) (%)	-	-	73	78	90
Coal consumption (MJ/ton_{clk})	3135	3241	3135	3135	7100
NG consumption (MJ/ton_{clk})	0	0	1859	0	0
Power consumption (MJ/ton_{clk})	474	474	723	1491	1431
Power generation (MJ/ton_{clk})	0	0	0	0	-1223
Clinker production (t_{clk}/h)					117.7
CO_2 from raw meal calcination (tCO_2/h)					67.3
CO_2 capture efficiency of carbonator (%)					90.0

The *CCR* is based on the amount of CO_2 captured by the process over the total CO_2 generated, which is from the kiln and by the fuel combustion internally in the capture process. Because of this, there is an unknown for the CaL technology.

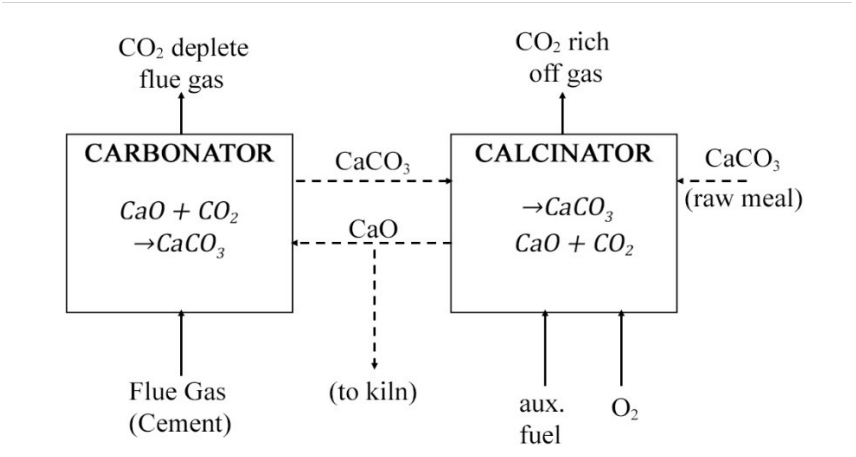


Figure 2.1 - *Calcium Looping capture CO2 system scheme (ECRA, CEMCAP, 2018)*

In the calcium looping, additional coal is burnt in the cement plant, and from Figure 2.1, the flue gas from the cement plant is sent to the carbonator which has an exchange with the calcinator in which more limestone is heated releasing more CO_2. Because of this, the *CCR* is based on the amount captured considering the additional fuel required by the CaL process. Oppositely, the CAP and MAL technologies have their *CCR* based on the amount captured from the flue gas which is the same for every case. Therefore, for the model, it will be used the CO_2 avoided from the flue gases as efficiency to have a fair comparison between the capture options.

Table 2.2 – *Values of the calculated additional emissions [t emitted/t captured], efficiency [%] and specific cost for every capture technology [€/t]*

	$\Delta E_{k,t}^{gas}$	$\Delta E_{k,t}^{coal}$	$\Delta E_{k,t}^{el,ren}$	$\Delta E_{k,t}^{el,mix}$	$\Delta E_{k,t}^{el,NGCC}$	$\Delta E_{k,t}^{el,coal}$	**η**	**cost**
	[t/t]	[t/t]	[t/t]	[t/t]	[t/t]	[t/t]	[%]	[€/t]
CAP	0.137	0	0	0.0233	0.0359	0.081	90	66.2
MAL	0	0	0	0.0951	0.147	0.333	90	85.3
CaL	0	0.073	0	0.0253	0.029	0.066	91	52.4

In Table 2.2 all the calculated values of the additional emissions are reported, with the efficiency and specific cost of each technology. From these data it is possible to do some important considerations. The MAL technology has the highest indirect emissions but no direct emissions, this means that in the case of using renewable energy, this technology would give zero additional emissions, however its cost is even the highest among them. On the other side, the CaL technology, not only has the highest efficiency but even the lowest cost, while its additional emissions are nearly the same as the MAL technology considering the Italian energy mix.

In the model, all the three technology will be given as options to select considering two different scenarios. One in which the additional emissions are calculated using the Italian energy mix, and one considering renewable energy. The other two emissions will not be considered since the performance of the capture technology would worsen a lot and because the CaL technology would always be selected since it would have even the lowest additional emissions.

Chapter 3

The CCS model

This chapter presents the main assumptions and the mathematical formulation of the CCS supply chain model. The model is implemented in GAMS (General Algebraic Modelling System) software and developed from a previous study described in d'Amore and Bezzo (2017).

3.1 Model assumptions

The model is developed in GAMS software as a MILP problem and optimised by aim of CPLEX solver. The objective is to design a CCS SC aimed to decrease the CO_2 emissions of the Italian cement industry over a time period of 20 years. This model will then provide as results the total cost (*TC* [€]) required and the final CO_2 net emission (*E*[ton of CO_2]) which correspond to the two objective variables to be minimised. The economic objective is to minimise *TC* under a set carbon reduction target α (i.e., ECO scenarios). On the other hand, the environmental objective minimises *E* (i.e., giving ENV scenarios). A bi-objective optimisation will be presented as well, aiming at minimising both costs and emissions to determine the best trade-off configurations between these two conflicting objectives (Table 3.1).

The following input data are given to the mathematical model:

- Geographical location of the cement plants and their yearly CO_2 emission level
- Geographical location of suitable sequestration sites and their storage capacity
- Sequestration cost based on quantity
- CO_2 capture technologies efficiencies and costs
- Pipeline transportation onshore and offshore costs based on transported flowrate and distance
- CO_2 emissions related to the pumping via pipeline
- Indirect emissions due to the operation of capture systems

With these inputs, the model structure can be divided into four main stages:

1. Capture problem
2. Transport problem
3. Sequestration problem
4. Emissions problem

The model outputs are:

- The cost related to each stage (i.e., capture, transport, sequestration)
- The optimal amount of CO_2 captured, sequestrated and any additional indirect emissions due to the operation of capture systems
- The optimal location of cement plants and sequestration sites
- The optimal setting of the transport infrastructure in terms of length and flowrates

Regarding the model computational performance these parameters are taken into consideration:

- Computational time
- Relative error
- Number of equations and variables

As for the relative error between the relaxed optimal solution and best MILP solution, any result must be lower, at least, of 1% to be considered acceptable.

3.2 CO_2 emission sources

The location and level of emissions of Italian cement plants were obtained from E-PRTR (European Pollutant Release and Transfer Register) database. The register contains all the annual reports about the pollutant emissions from more than 3000 industrial facilities in all European Union Member States (EEA, 2020) updated to 2017.
From the Sustainability Report of 2017 from AITEC (Associazione Italiana Tecnico Economica del Cemento), it was stated that 29 cement plants were operative in 2017 and in fact the register gave 29 results that are reported in Table 3.1 and represented in Figure 3.1.

Table 3.1 – *Yearly CO_2 emission amount and position of each node in 2017*

n	Region	City		CO2 [kt/year]	Latitude	Longitude
1	PIEMONTE	ROBILANTE	CN	733	44.3	7.5
2	LOMBARDIA	CARAVATE	VA	471	45.88	8.66
3	LOMBARDIA	TERNATE	VA	529	45.78	8.68
4	LOMBARDIA	CALUSCO D'ADDA	BG	769	45.68	9.46
5	LOMBARDIA	TAVERNOLA BERGAMASCA	BG	360	45.71	10.03
6	LOMBARDIA	REZZATO	BS	932	45.51	10.34
7	FRIULI-VENEZIA-GIULIA	FANNA	PN	380	46.17	12.74
8	VENETO	PEDEROBBA	TV	319	45.87	11.96
9	VENETO	MONSELICE	PD	371	45.25	11.75
10	EMILIA-ROMAGNA	PIACENZA		311	45.04	9.71
11	EMILIA-ROMAGNA	VERNASCA	PC	427	44.77	9.8
12	TOSCANA	RASSINA	RA	351	43.65	11.83
13	TOSCANA	GREVE-TESTI	FI	269	43.61	11.28
14	UMBRIA	GUBBIO	PG	562	43.36	12.54
15	UMBRIA	SPOLETO	PG	219	42.74	12.67
16	UMBRIA	GUBBIO-GHIGIANO	PG	454	43.28	12.61
17	LAZIO	GUIDONIA-MONTECELIO	RM	514	42.005	12.71
18	LAZIO	COLLEFERRO	RM	322	41.73	13.006
19	ABRUZZO	CAGNANO AMITERNO	AQ	191	42.46	13.25
20	MOLISE	SESTO CAMPANO	IS	434	41.44	14.06
21	CAMPANIA	MADDALONI	CE	414	41.05	14.37
22	SARDEGNA	SAMATZAI	CA	283	39.46	9.02
23	PUGLIA	BARLETTA	BA	306	41.31	16.28
24	PUGLIA	GALATINA	LE	209	40.16	18.19
25	BASILICATA	BARILE	PZ	258	40.95	15.67
26	BASILICATA	MATERA		499	40.67	16.65
27	SICILIA	ISOLA DELLE FEMMINE	PA	257	38.19	13.24
28	SICILIA	AUGUSTA	SR	479	37.19	15.18
29	SICILIA	RAGUSA		285	36.9	14.72

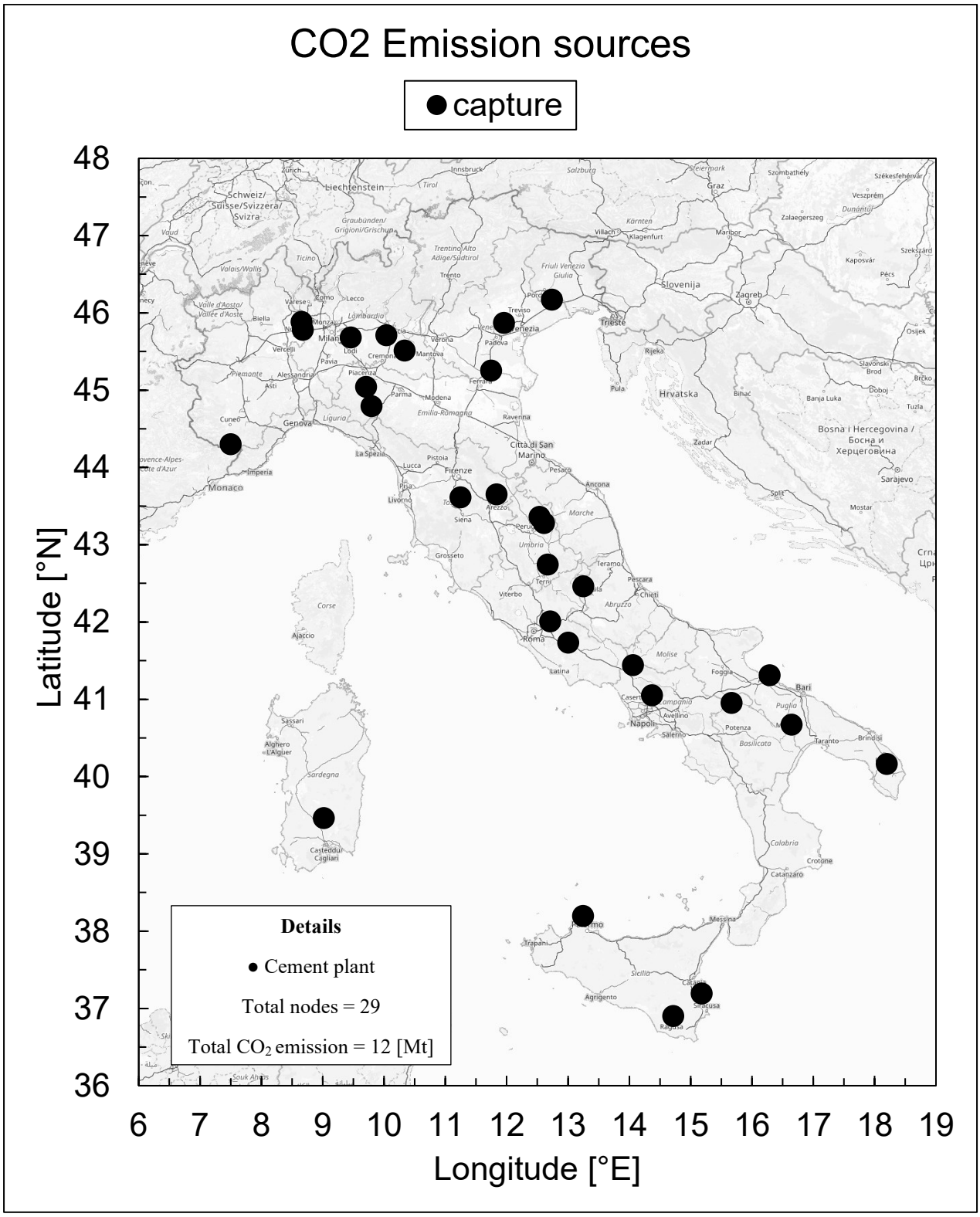


Figure 3.1 – *Geographical position of capture nodes*

3.3 Sequestration sites

As for sequestration stage, CO_2 sequestration is the injection of captured flowrates into suitable geological formations, such as deep saline aquifers, depleted oil and gas fields and unminable coal seams, for significant periods of time (thousands to millions of years) (IPCC, 2005). The EU GeoCapacity Project (2009) identified all the possible sequestration sites in Europe and in its Storage capacity report (EU GeoCapacity Project, 2009), the aquifers are the most promising option since they have the highest storage capacity. Donda et al. (2010) estimated the potential CO_2 storage capacity of 14 Italian deep saline aquifers, which should be able to contain the entire volume of CO_2 emitted in Italy for at least the next fifty years. (Figure 3.2)

Table 3.2 – *Potential Italian sequestration sites, position, capacity and depth.*

n	Site name	Longitude	Latitude	Capacity [Mt]	Average depth [m]	Offshore
101	Lombardia 1	9.38	45.39	76	1590	NO
102	Lombardia 2	10.88	45.28	356	1100	NO
103	Emilia 1	11.56	44.66	492	1100	NO
104	Emilia Mare	13.23	44.04	1314	1400	YES
105	Marche 1	13.2	43.59	716	1270	NO
106	Abruzzi 1	13.91	42.68	46	1340	NO
107	Abruzzi 2	14.31	42.25	80	1320	NO
108	Abruzzi 3	14.52	42.13	30	1360	NO
109	Abruzzi mare	14.77	42.72	1300	1500	YES
110	Molise 1	15.03	41.87	32	1320	NO
111	Molise 2	15.05	41.74	140	1260	NO
112	Bradanica	16.55	40.43	688	1000	NO
113	Calabria ionica	17.14	39.22	420	1280	YES
114	Sicilia 1	12.51	37.84	206	1050	NO

The capacity is taken from the results of Donda et al. (2010) considering a storage efficiency factor of 2% as suggested from the EU GeoCapacity project, that gives a total storage capacity of 5900 [Mt] (Table 3.3).

Given the scale of this optimisation, sequestration sites will be here treated as local nodes rather than areas, assuming to inject the CO_2 in the centre of the considered basins.

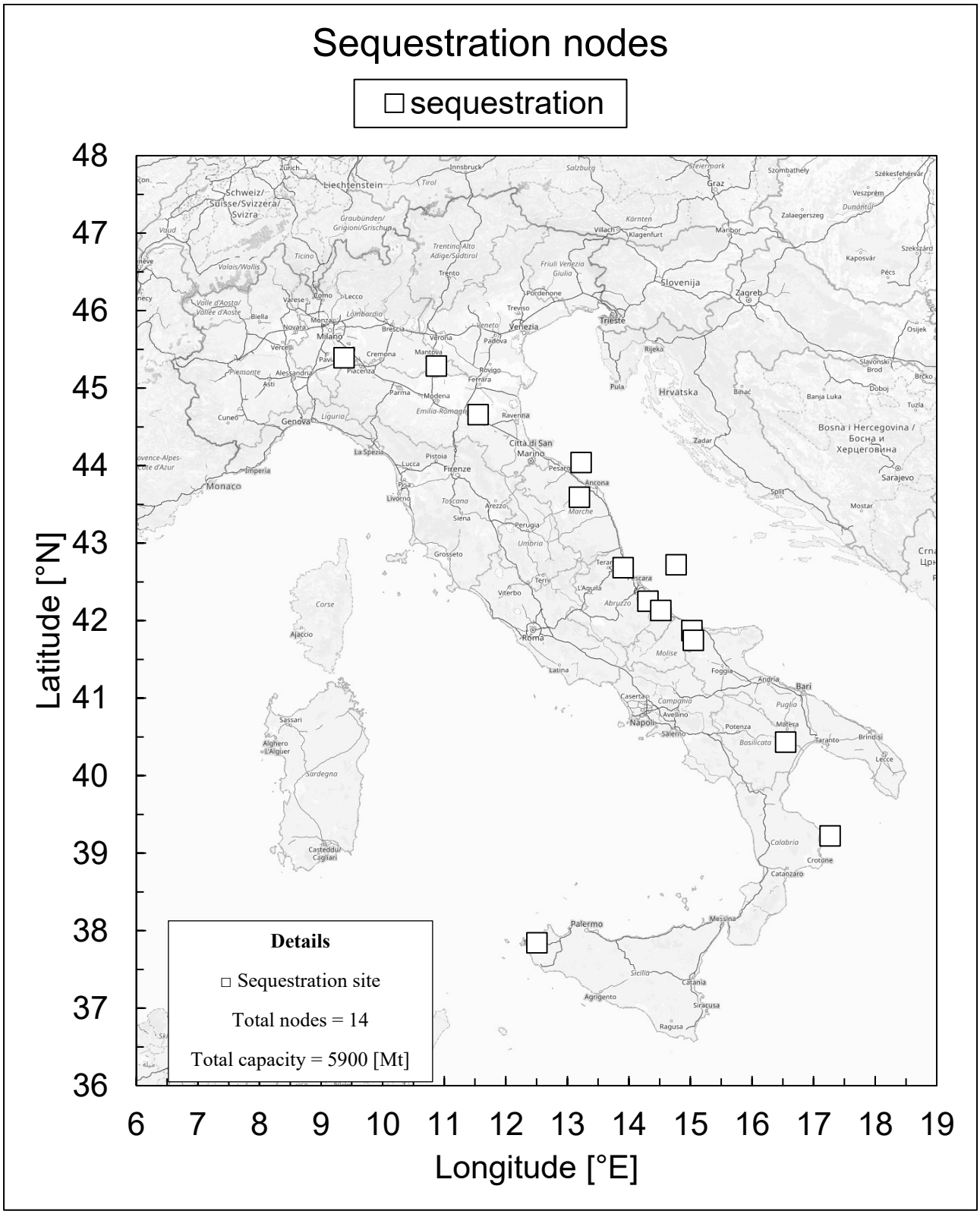


Figure 3.2 – *Geographic position of sequestration nodes*

3.4 Clustering

To reduce the computational burden and to determine a more geographically realistic representation of the SC, a clustering approach is applied among the capture nodes. The method used is a k-mean clustering through MATLAB software. The k-mean method classifies a given data set through a certain number of clusters *k* assumed a priori. Each cluster will have a centroid and its position is calculated using an interactive algorithm (MacQueen, 1967). The process will be:

1. Choosing an initial *k* cluster centres (centroids)
2. Calculating the distance between each point *n* of the data set to each centroid.
3. Assigning each point to the nearest centroid until there is no more points pending.
4. New *k* centroids will be re-calculated as barycentres from the previous step.
5. A new assigning between the points and the new centroids is done.
6. Repeating from step 3 to step 5 will change the position of the centroids at every new loop.
7. Convergence is reached when there are no more changes in the centroids position.

The algorithm aims at minimizing an objective function which is a squared error function:

$$J = \sum_{j=1}^{k} \sum_{i=1}^{n} \left\| x_i^{(j)} - c_j \right\|^2 \tag{3.1}$$

The norm calculates the distance measure between a data point $x_i^{(j)}$and the centroid c_j.

With this method, each cluster has a centre (centroid), where the locally sourced CO_2 will be conveyed and from where a sum of local flowrates will be sent to sequestration. As a result, CO_2 transport is divided into two consequential phases: intra-connection among cement plants and centroids (local transport), and inter-connection among centroids and sequestration basins. For the model, three number of clusters were chosen, hence, three possible case studies are investigated: 5 clusters (Figure 3.3), 8 clusters (Figure 3.4) and 10 clusters (Figure 3.5).

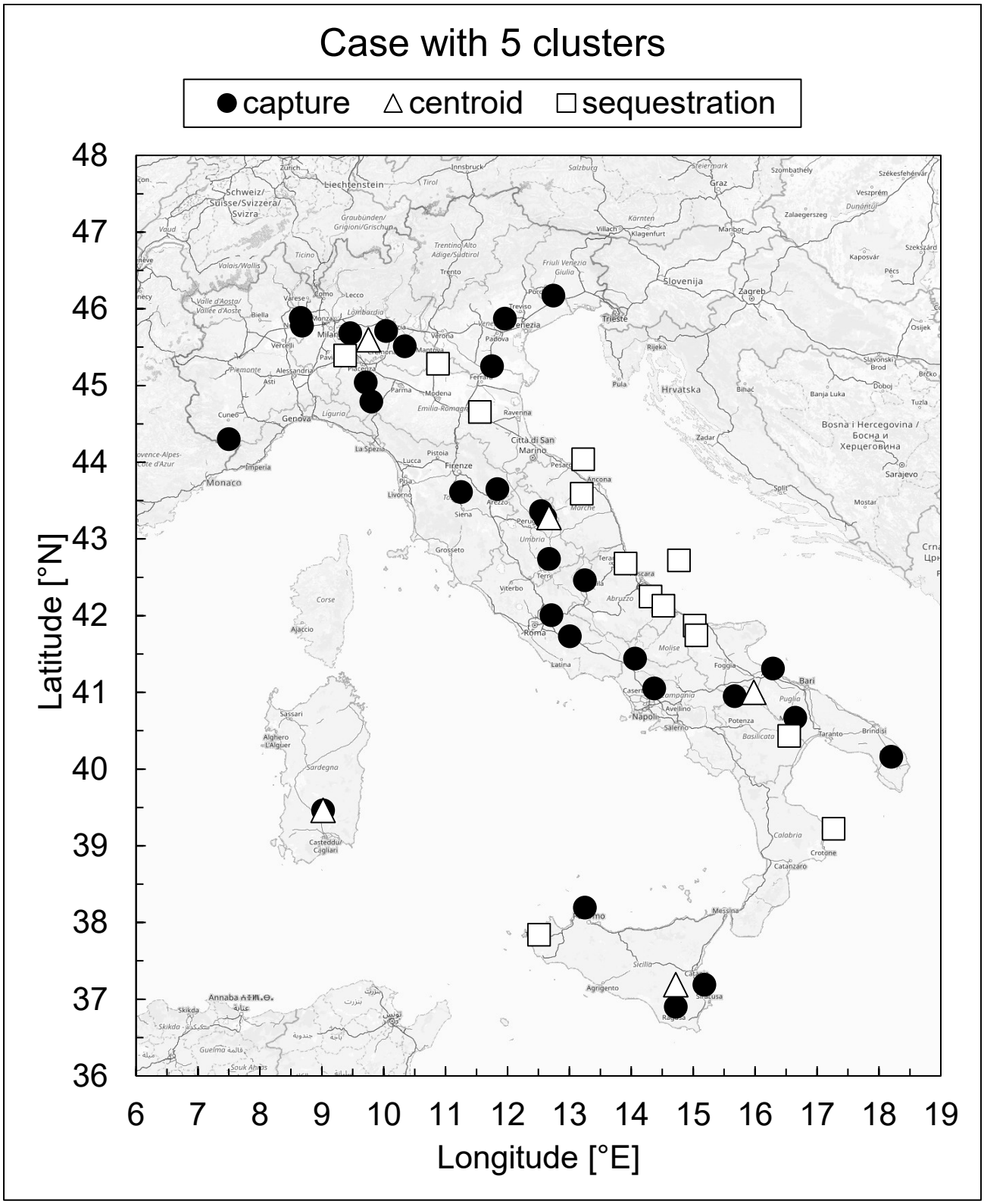


Figure 3.3 – *Map of all the nodes and centroids for the case with 5 clusters.*

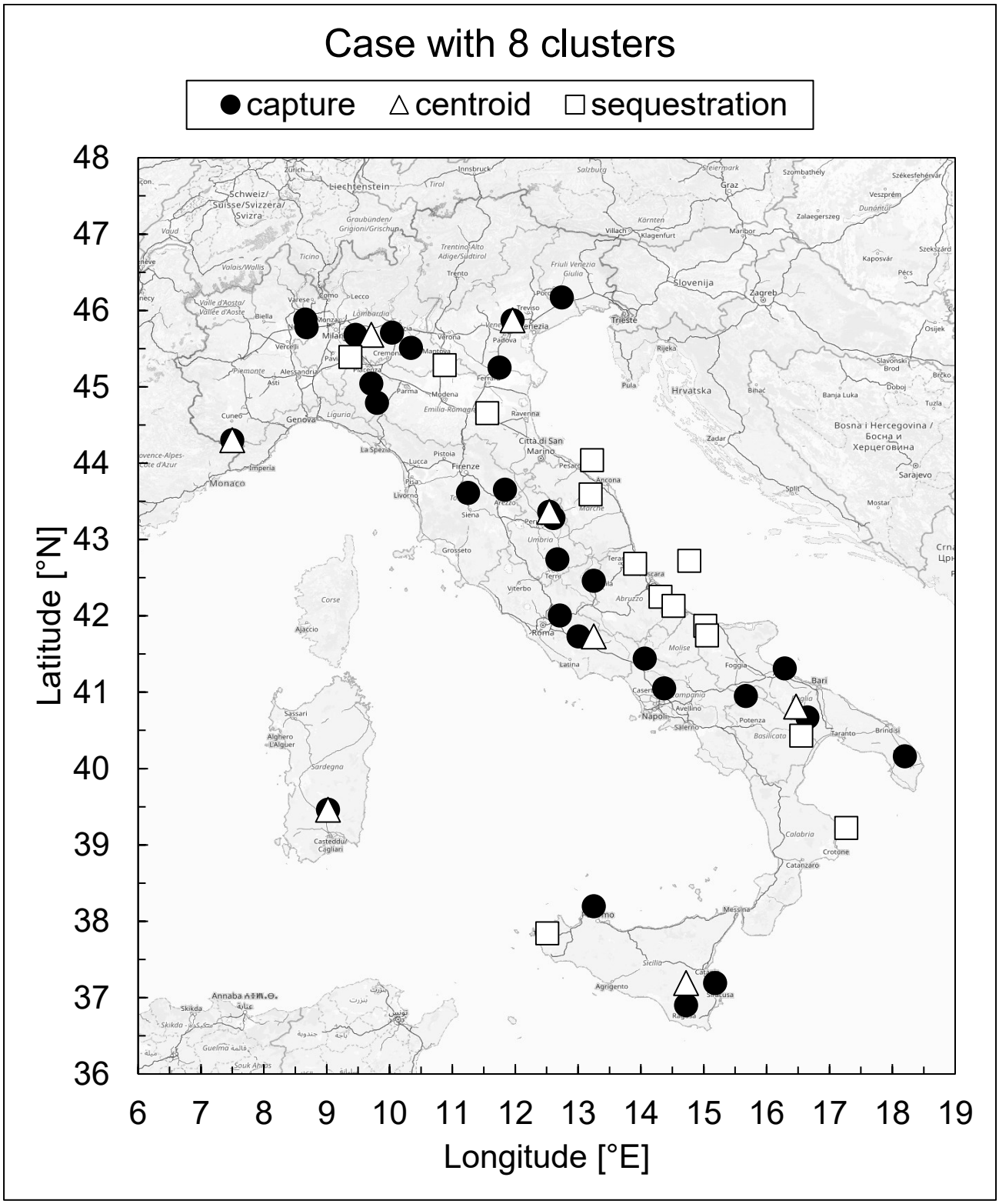


Figure 3.4 – *Map of all the nodes and centroids for the case with 5 clusters*

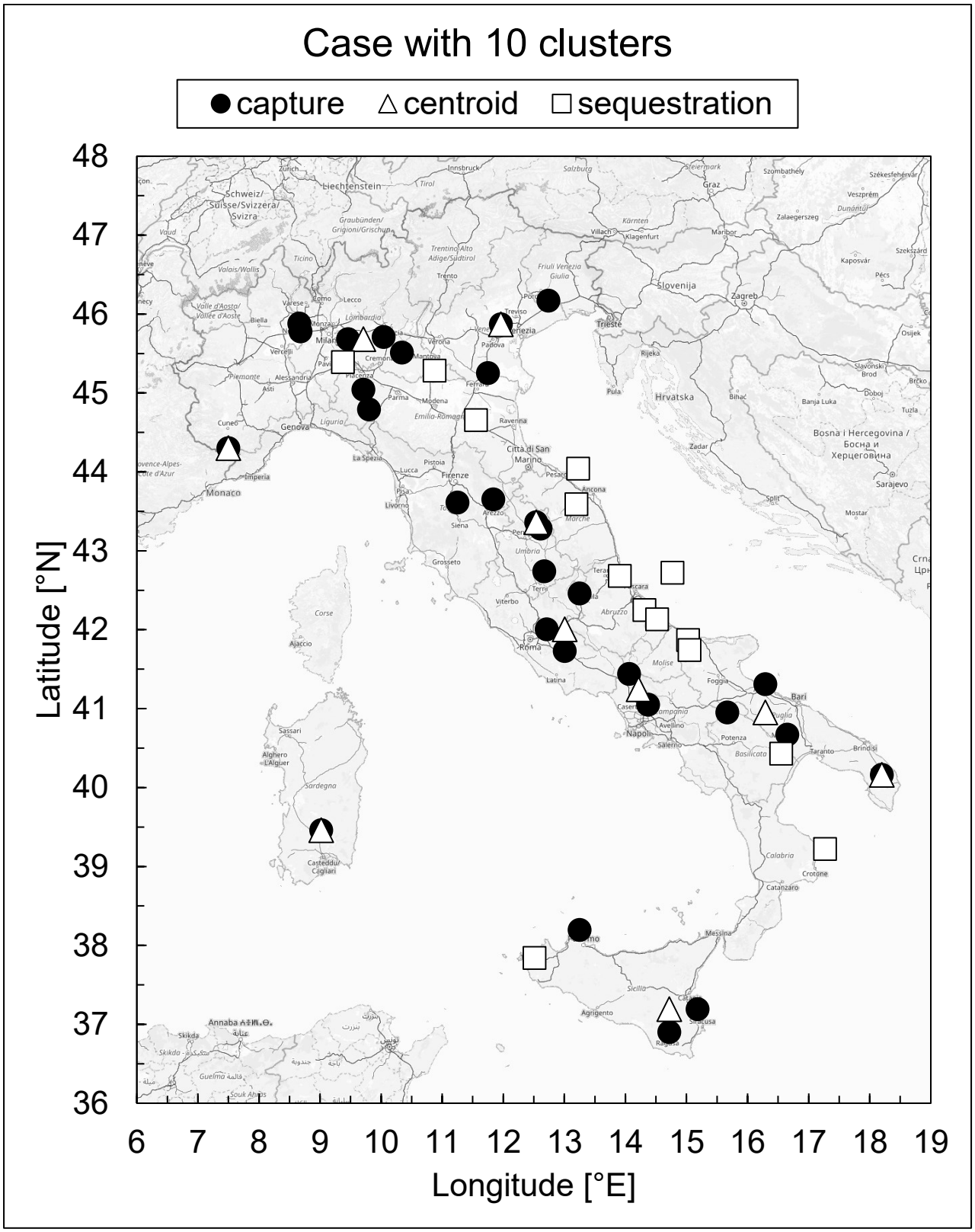


Figure 3.5 – *Map of all the nodes and centroids for the case with 5 clusters.*

3.5 Mathematical Formulation

This section will describe the mathematical formulation of the model. The model for all the single-objective cases (ECO and ENV) has the same balances and constraints, while the MULTI case will present an additional part for combining the objective functions.

3.5.1 Input data

The model is based on the following sets.

- $c = \{c_{1\text{-}X}, c_{101\text{-}114}\}$ = centroids and sequestration nodes, with X = {5; 8; 10} accordingly to the subcase considered.
- $k = \{k_{1\text{-}3}\}$ = the three capture technologies: CAP, MAL and Ca-L.(*link to chapter 2*)
- $n = \{n_{1\text{-}29}, n_{101\text{-}114}\}$ = all the 43 nodes in the model.
- $p = \{p_{1\text{-}4}\}$ = flowrates, describing four possible discrete capacities for the pipelines.
- $cluster^C = \{c_{1\text{-}X}\}$ = a subset of c without the sequestration nodes
- $seque^C = \{c_{101\text{-}114}\}$ = a subset of c describing the sequestration clusters only
- $seque^N = \{n_{101\text{-}114}\}$ = a subset of n describing the sequestration nodes only
- t = {1-20} = time interval considered, in years.

The subsets $seque^C$ and $seque^N$ are coincident, since no clustering was operated on storage nodes thus, each basin corresponds to a cluster.

Linear distances were evaluated by using the spherical law of cosines reported in d'Amore and Bezzo (2017) which considers the Earth spherical, ignoring the ellipsoidal effects:

$$LD_{x,y} = \cos^{-1}[\sin(lat^x) \cdot \sin(lat^y) + \cos(lat^x) \cdot \cos(lat^y) \cdot \cos(long^x - long^y)] \cdot R \quad (3.2)$$

Eq.(3.2) gives the distance between the points x and y with errors up to 0.3% and R is the radius of the Earth equal to 6372.785 km. For each subset $LD_{x,y}$ has to be calculated for both the intra and inter connections.

As for transport, onshore (UTC_p^{on}[€/km/t]) and offshore (UTC_p^{off}[€/km/t]) pipeline transport costs were discretised into four intervals of flowrates (Q_p^{min} [kt]; Q_p^{max} [kt]) to decrease the computational complexity (Table 3.3).

Table 3.3 – *Flowrate capacities with respective onshore and offshore costs.*

Flowrate	**P1**	**P2**	**P3**	**P4**
Q_p^{min} [kt]	150	320	550	1000
Q_p^{max} [kt]	320	550	1000	5000
UTC_p^{on}[€/km/t]	0.108	0.073	0.050	0.022
UTC_p^{off}[€/km/t]	0.224	0.141	0.091	0.034

The minimum and maximum of all capacities are based on the lowest single flowrate obtainable from a node and the maximum flowrate from the centroids. In particular, *UTC* was calculated from d'Amore and Bezzo(2017) and updated with the chemical engineer plant costs indexes (CEPCI, 2018). To distinguish between an onshore or offshore transport, the parameter $F_{c,cp}$ was estimated:

$$F_{c,cp} = F_c + F_{cp} \tag{3.3}$$

The indexes of $F_{c,cp}$ refer the transport which starts from node c and arrives in node cp. F_c and F_{cp} can only assume the values of 0 for when the node is onshore or 1 when it is offshore. Since the nodes offshore are only meant for sequestration, and any transport that starts from those nodes is not allowed, this means their sum will be either 0 or 1 identifying the transport as onshore or offshore.

In regard to the sequestration costs, an average unitary sequestration cost (*USC* [€/t]) is considered and is equal to 7.20 € for 1 ton of captured CO_2 to be sequestrated onshore. It was calculated from d'Amore and Bezzo (2017) and updated with the chemical engineer plant costs indexes (CEPCI, 2018). As for offshore sequestration, its cost is estimated to be 2.5 times higher than the onshore alternative (ZEP, 2011). This additional offshore transport cost is implemented in the model through the parameter off_c which is set equal to 1 if c is onshore and 2.5 if c is offshore.

In the ENV cases optimisation, costs would be ignored if they were not related to any emission. To keep the ENV cases bounded on the economic side too and avoid unrealistic results, the CO_2 released due to the pumping in the pipelines of the captured CO_2 is considered (E^{pump}[gCO_2/t/km]). This is a scalar estimated on the work of Zhang et al., (2006) in which it is

reported that for every 100 km of pipeline there is an energy requirement of 8.3 [kJ/kgCO_2]. Calculating the specific consumption over 1 km, and multiplying the value for the carbon intensity of the Italian energy mix, E^{pump} will result equal to 5.91 grams of CO_2 released for 1 t of CO_2 captured transported for 1 km. This value is fixed for both scenarios, since it is assumed the use of renewable energy in scenario B only for the capture technologies.

About the flowrates, the efficiencies of all the capture technologies are known and are similar (90~91%) (*link to chapter 2)*. The parameter $z_{n,p}$ is introduced to associate flowrates p to capture nodes n. When there will be a capture in a node n, $z_{n,p}$ will be equal to 1 for the respective flowrate p identifying the interval in which the amount falls (Table 3.4).

Table 3.4 – $z_{n,p}$ *values for all the capture nodes*

n	P1	P2	P3	P4
1	0	0	1	0
2	0	1	0	0
3	0	1	0	0
4	0	0	1	0
5	0	1	0	0
6	0	0	1	0
7	0	1	0	0
8	1	0	0	0
9	0	1	0	0
10	1	0	0	0
11	0	1	0	0
12	0	1	0	0
13	1	0	0	0
14	0	1	0	0
15	1	0	0	0
16	0	1	0	0
17	0	1	0	0
18	1	0	0	0
19	1	0	0	0
20	0	1	0	0
21	0	1	0	0
22	1	0	0	0
23	1	0	0	0
24	1	0	0	0
25	1	0	0	0
26	0	1	0	0
27	1	0	0	0
28	0	1	0	0
29	1	0	0	0

3.5.2 Objective functions

The model is optimised under the following objective:

$$objective = min(sel^{OBJ} \cdot TC + (1 - sel^{OBJ}) \cdot E) \quad (3.4)$$

In Eq. (3.4) sel^{OBJ} is a parameter that can assume the value of 0 or 1. Based on the value given the model will perform an environmental optimisation for 0 or an economic optimisation for 1.

$$TC = TCC + TTC + TSC \quad (3.5)$$

TC [€] is the total cost and is given from the sum of TCC [€] (total capture cost), TSC [€] (total transport cost) and TSC [€] (total sequestration cost). This is the equation that will be minimised in all ECO cases.

$$E = E^0 - E^{out} + \Delta E + E^{pump,tot} \quad (3.6)$$

E[ton of CO_2] is the final CO_2 net emission obtained applying the CCS SC, E^0 [tCO_2] is initial total amount of CO_2 from the capture nodes, E^{out} [tCO_2] is the total CO_2 sequestrated which is equal to the captured one, ΔE [tCO_2] is the total additional CO_2 emission due to the use of the capture technologies, $E^{pump,tot}$ [tCO_2] is the total amount of CO_2 release due to the pumping in the pipelines. In all ENV cases E will be minimised.
All the variables are the final and total ones, meaning TC and E are the total cost and final CO_2 net emission after the time period of 20 years considered.

3.5.3 The capture problem

The capture problem consists in the selection of the nodes and technology where to capture the CO_2. The total yearly emission is:

$$E_t^0 = \sum_n E_{n,t}^{in,max} \tag{3.7}$$

Eq. (3.7) calculates the total initial emission of CO_2 E_t^0 [tCO_2] in year *t* from the summation of the maximum CO_2 emission of each capture node $E_{n,t}^{in,max}$[tCO_2].

$$E_{k,n,t}^{in,CAPT} = \eta_k \cdot E_{n,t}^{in,max} \cdot \gamma_{k,n} \tag{3.8}$$

$E_{k,n,t}^{in,CAPT}$ [tCO_2] is the amount of CO_2 captured in node *n*, in year *t* with technology *k.* η_k is the efficiency of the capture technology *k* chosen, $E_{n,t}^{in,max}$ [tCO_2] is the yearly emission of CO_2 in node *n* and $\gamma_{k,n}$ is a binary variable equal to 1 when the technology *k* in node *n* is chosen and equal to 0 otherwise.

$$E_{c,t}^{in} = \sum_{k,n} NC_{n,c} \cdot E_{k,n,t}^{in,CAPT} \tag{3.9}$$

$E_{c,t}^{in}$ [ton of CO_2] is the total amount of CO_2 captured in cluster *c* in year *t*, which is equal of the summation of $E_{k,n,t}^{in,CAPT}$ [tCO_2] per $NC_{n,c}$ a parameter equal to 1 when *n* belongs to *c*, or 0 otherwise.

$$TCC_t = \sum_{k,n} E_{k,n,t}^{in,CAPT} \cdot UCC_k \tag{3.10}$$

TCC_t [€] is the total capture cost in year *t* and it is equal to the sum of the captured CO_2 in every node multiplied for UCC_k[€/tCO_2] the unitary capture cost of technology *k* (*link to chapter 2)*. This means the capture cost depends on the amount of CO_2 captured and the cost of the technology used.

$$\sum_k \gamma_{k,n} \leq 1 \tag{3.11}$$

Eq. (3.11) is a constraint that at maximum one capture technology *k* can be installed and operated in a node *n*.

3.5.4 The transport problem

The transport problem defines the infrastructure of the CCS SC. It consists in two parts: the intra connections and the inter connections.

$$E_{c,t}^{in} + \sum_{p,cp} Q_{p,cp,c,t}^{C} = E_{c,t}^{out} + \sum_{p,cp} Q_{p,c,cp,t}^{C} \quad (3.12)$$

Eq. (3.10) is a mass balance and constraint on all the transported CO_2. $E_{c,t}^{in}$ [tCO_2]is the amount of captured CO_2 from the nodes and sent to the cluster *c* in year *t*, while $E_{c,t}^{out}$[tCO_2] is the amount of CO_2 sequestrated in cluster *c* in year *t*. $Q_{p,cp,c,t}^{C}$ [tCO_2] and $Q_{p,c,cp,t}^{C}$[tCO_2] are the flowrates, the former with capacity *p*, from cluster *cp* to cluster *c* in year *t*, while the latter is the same but from cluster *c* to cluster *cp*. This means that all the CO_2 from the centroid must be sequestrated.

$$Q_{p,n,c,t}^{N} = \sum_{k} E_{k,n,t}^{in,CAPT} \cdot z_{n,p} \cdot NC_{n,c} \quad (3.13)$$

$Q_{p,n,c,t}^{N}$ [tCO_2] is the intra connection flowrate of capacity *p*, from node *n* to cluster *c* in year *t*, and it is equal to summation of $E_{k,n,t}^{in,CAPT}$[tCO_2] for all technologies *k*, multiplied for $NC_{n,c}$ and $z_{n,p}$ which identifies the flowrate *p* from node *n*.

$$Q_{p,c,cp,t}^{C} \leq \lambda_{p,c,cp,t}^{C} \cdot Q_{p}^{max} \quad (3.14)$$

$$Q_{p,c,cp,t}^{C} \geq \lambda_{p,c,cp,t}^{C} \cdot Q_{p}^{min} \quad (3.15)$$

Eq. (3.14) is an upper bound where the flowrate $Q_{p,c,cp,t}^{C}$ [tCO_2] must be lesser or equal of the maximum flowrate *p*, and $\lambda_{p,c,cp,t}^{C}$ is a binary variable that assume the value of 1 when there is the transport between *c* and *cp*, and 0 where there is no transport. On the other hand Eq. (3.15) is the lower bound, like for Eq.(3.14) the flowrate must be greater or equal to the minimum one available.

$$TTC_{c,t}^{intra} = \sum_{p,n} Q_{p,n,c,t}^{N} \cdot LD_{n,c}^{intra} \cdot UTC_{p}^{on} \quad (3.16)$$

$$TTC_t^{intra} = \sum_c TTC_{c,t}^{intra} \tag{3.17}$$

Eq. (3.16) gives $TTC_{c,t}^{intra}$ [€], the total transport cost of the intra connections in cluster *c* in year t. It is the summation of the product of UTC_p^{on} (Table 3.3) with $Q_{p,n,c,t}^N$ and $LD_{n,c}^{intra}$ [km] which is the linear distance of the intra connection between the node *n* and cluster *c*. The sum of $TTC_{c,t}^{intra}$ for all clusters gives the total transport cost at year *t* (TTC_t^{intra} [€]) in eq. (3.17).

$$TTC_t^{inter} = \sum_{p,c,cp} Q_{p,c,cp,t}^C \cdot LD_{c,cp}^{inter} \cdot \left(\left(1 - F_{c,cp}\right) \cdot UTC_p^{on} + F_{c,cp} \cdot UTC_p^{off}\right) \tag{3.18}$$

TTC_t^{inter}[€] is the total transport cost of all the inter connections in year *t* and it is given from the summation of the product between $Q_{p,c,cp,t}^C$, $LD_{c,cp}^{inter}$ [km] is the linear distance between *c* and *cp*, UTC_p^{on}[€/km] and UTC_p^{off} [€/km] the unitary offshore transport cost of flowrate *p*. $F_{c,cp}$ is a parameter equal to 0 when the transport is onshore and equal to 1 when it is offshore.

$$TTC_t = TTC_t^{intra} + TTC_t^{inter} \tag{3.19}$$

The sum of the total intra transport cost and the total inter transport cost gives the total transport cost TTC_t [€].

$$E_t^{C,pump} = \sum_{p,c,cp} Q_{p,c,cp,t}^C \cdot LD_{c,cp}^{inter} \cdot E^{pump} \tag{3.20}$$

$$E_t^{N,pump} = \sum_{p,c,cp} Q_{p,n,c,t}^N \cdot LD_{n,c}^{intra} \cdot E^{pump} \tag{3.21}$$

$$E_t^{pump,tot} = E_t^{N,pump} + E_t^{C,pump} \tag{3.22}$$

Eq. (3.20) and (3.21) calculate the additional emission for the inter ($E_t^{C,pump}$[tCO_2]) and intra ($E_t^{N,pump}$[tCO_2]) transports via pipeline which is given by the flowrate *Q* multiplied for the linear distance between the two nodes and for E^{pump}. Their sum in Eq. (3.22) gives the total amount of

CO_2 emission related to the pumping. With Eq.(3.20) and (3.21) CO_2 emissions of the transport stage are bounded with costs, since the flowrate Q is associated to *UTC* (Table 3.3).

$$\sum_p \lambda^C_{p,c,cp,t} \leq 1 \tag{3.23}$$

Eq. (3.23) is a constraint on the chosen flowrate *p* that must be only one for each inter connection. In short when the CO_2 is transported to the sequestration only one flowrate is allowed.

$$Q^N_{p,n,c,t} \geq Q^N_{p,n,c,t-1} \tag{3.24}$$

$$Q^C_{p,c,cp,t} \geq Q^C_{p,c,cp,t-1} \tag{3.25}$$

Eq. (3.24) and (3.25) are constraints made to avoid possible gaps or different choices in the planning and operation of the infrastructure throughout the years. When there is a flowrate of captured CO_2 from one node, this must continue through the years and must be constant. Since the yearly amount of CO_2 from every node is constant, and the technology chosen is only one, there cannot be different flowrates for the same *n* and *c*, and between *c* and *cp* in different years *t.*

3.5.5 The sequestration problem

$$E^{out,max}_c \leq \sum_t E^{out}_{c,t} \tag{3.26}$$

$E^{out}_{c,t}$ [tCO_2] is the amount of CO_2 sequestrated in cluster *c* at year *t*. $E^{out,max}_c$[tCO_2] is the upper storage limit of cluster *c*. It is not possible to inject an amount bigger than the maximum one allowed in.

$$E^{out}_t = \sum_c E^{out}_{c,t} \tag{3.27}$$

E^{out}_t [ton of CO_2] is the total CO_2 sequestrated in all clusters in year *t.*

$$TSC_t = \sum_c E_{c,t}^{out} \cdot USC \cdot off_c \quad (3.28)$$

TSC_t[€] is the total sequestration cost at year *t* and it is given from the summation of all clusters of $E_{c,t}^{out}$ multiplied for USC and off_c already described in Section 3.5.1.

3.5.6 The emissions problem

Operating capture requires energy and material which determine the generation of additional emissions related to capture itself(*this part must be linked with chapter 2).* This stage consists in determining these additional emissions.

$$E_t \leq (1 - \alpha) \cdot E_t^0 \quad (3.29)$$

Eq. (3.29) describes of how much the model should decrease the initial emission E_t^0 [tCO_2] at year *t.* α is a fixed value and it is the carbon reduction target that must be achieved. E_t [tCO_2] is the final net CO_2 emission that remains after the capture and sequestration process.
Changing the value of α gives different subcases for ECO. The main value will be 50% but values of 30% and 70% will be investigated.

$$\Delta E_t = \Delta E_t^{heat} + \Delta E_t^{el} \quad (3.30)$$

ΔE_t [tCO_2] is the additional emission of CO_2 to the use of the capture technology in year *t*. It is the sum of the direct emissions produced by consuming a fuel (ΔE_t^{heat}) and the indirect emissions due the consumption of electricity (ΔE_t^{el}).

$$\Delta E_t^{heat} = \Delta E_t^{gas} + \Delta E_t^{coal} \quad (3.31)$$

ΔE_t^{heat} is given by the sum of the direct emission due the combustion of natural gas (ΔE_t^{gas}[tCO_2]) or coal (ΔE_t^{coal}[tCO_2]).

$$\Delta E_t^{gas} = \sum_{k,n} E_{k,n,t}^{in,CAPT} \cdot \Delta E_{k,t}^{gas} \quad (3.32)$$

$$\Delta E_t^{coal} = \sum_{k,n} E_{k,n,t}^{in,CAPT} \cdot \Delta E_{k,t}^{coal} \quad (3.33)$$

Both Eq. (3.32) and (3.33) are similar. The additional emission is calculated with the sum of all the technologies *k* in all nodes *n* of the product of the amount of CO_2 captured ($E_{k,n,t}^{in,CAPT}$) with $\Delta E_{k,t}^{gas}$ [tCO_2 released/tCO_2 captured] and $\Delta E_{k,t}^{coal}$ [tCO_2 released/tCO_2 captured] parameters that describe how much tons of CO_2 is produced for 1 ton of CO_2 captured with *k*.

$$\Delta E_t^{el} = \sum_{k,n} E_{k,n,t}^{in,CAPT} \cdot \Delta E_{k,t}^{el} \quad (3.34)$$

Eq. (3.34) calculates all the indirect emission due the consumption of electrical power. $\Delta E_{k,t}^{el}$ [tCO_2 released/tCO_2 captured] is a parameter related to the carbon intensity of the energy mix considered in the scenario analysed and the technology *k* used .(*this part must be linked with chapter 2).*

3.6 Multi-objective optimisation

Multi-objective case studies were optimised by aim of an ε-constrained looping solution method. This method consists in choosing one of the two objective functions as the only objective and transforming the remaining one into a constraint. With a systematic variation of the constraint bounds it is possible to obtain the elements that will build the Pareto front (Laumanns et al., 2006).

The first step is to define new set and subsets:

- o = {CO_2, cost}, respectively the E function and TC function.
- $o1_o$ = CO_2, first element of set o.
- $om1_o$ = cost, second element of set o.

The upper and lower bounds are required, and they will be called: $rhsmax_o$ and $rhsmin_o$. They are the results of Eq. (3.5) and eq (3.6) for both the ECO and ENV cases within the same subcase (i.e., 5 clusters, 8 clusters, 10 clusters) and scenario.

Lastly, new variables are needed: sl_o the surplus variable that can be arbitrarily chosen, $objmax_o$ the upper limit and $objmin_o$ the lower limit. Now it is possible to write the equations and inequation of the method:

$$obj_{om1} \leq objmax_{om1} \tag{3.35}$$

$$obj_{om1} \geq objmin_{om1} \tag{3.36}$$

$$obj_{om1} = rhsmin_{om1} + (rhsmax_{om1} - rhsmin_{om1}) \cdot sl_{om1} \tag{3.37}$$

$$obj_{om1} = rhsmin_{om1} + (rhsmax_{om1} - rhsmin_{om1}) \cdot (sl_{om1} - 0.001) \tag{3.38}$$

$$obj_{o1} = objective \tag{3.39}$$

Eq. (3.35) and eq. (3.36) are the limits in which the method will search for the multi-objective solution. Eq. (3.37) and eq. (3.38) describe the variation of constraint bounds to find the solution. Eq. (3.39) is the free objective function. In this case the CO_2 function, E, is the free one, while the cost function, TC, is the constraint.

3.7 Scenarios description

Indirect emissions due to operation of capture systems are evaluated in Section 3.5.6 according to different carbon intensity scenarios (*link to chapter 2)*, which determine the choice of optimising different case studies based on the selection of these. In particular in Scenario A indirect emissions calculations are based on the Italian energy mix carbon intensity, while Scenario B will assume the use of renewable energy. The clustering described in Section 3.4 determines furthermore subcases to optimise in each Scenario.

Summarising, the model optimises two main scenarios based on the assumption on the energy mix associated to the indirect emissions due to capture: Scenario A (carbon intensity of Italian energy mix) and Scenario B (carbon intensity of renewable-based energy mix). Each scenario is optimised in economic terms (ECO), environmental terms (ENV) or through a multi-objective approach (MULTI). Each optimisation is further decomposed into three additional subcases depending on the choice in the number of cluster (5,8 or 10 clusters). A summary of all the investigated case studies is reported in Table 3.5

Table 3.5 – *Summary of all investigated scenarios and cases*

Scenario	Case	Sub-Case	Short Name
A (Italian average electric mix)	ECO	5	A.ECO.5
		8	A.ECO.8
		10	A.ECO.10
	ENV	5	A.ENV.5
		8	A.ENV.8
		10	A.ENV.10
	MULTI	5	A.MULTI.5
		8	A.MULTI.8
		10	A.MULTI.10
B (renewable energy)	ECO	5	B.ECO.5
		8	B.ECO.8
		10	B.ECO.8
	ENV	5	B.ENV.5
		8	B.ENV.8
		10	B.ENV.10
	MULTI	5	B.MULTI.5
		8	B.MULTI.8
		10	B.MULTI.10

Chapter 4

Results and discussion

The results obtained from optimisation of all cases listed in Table 3.5 are presented and commented in this chapter. All the solutions are presented following the order discussed in the previous chapter therefore, starting with the ECO cases, then the ENV cases and lastly the MULTI cases. For each subcase, the final costs and emissions are provided, and for ECO and ENV cases, the configuration of SC is represented on a map to show all the intra and inter connections among nodes, while for the MULTI cases, a Pareto front (Section 3.6) is shown to discuss the conflict between environmental and economic objectives. At the end the computational performance of the model will be evaluated through the model statics

4.1 Economic optimisations

In this section all the economic optimisations are described in detail. The aim of the model is to minimise *TC* given by Eq. (3.5) and the best solution will be considered the one with the lowest total cost. In the possibility there are two subcases with the same *TC*, the one with the lowest emissions will be regarded as best one. In fact, for this case study a carbon reduction α must be set and achieved, and three different values are selected for a sensitivity analysis: 30%, 50% and 70%. The case with α equal to 50% is regarded as base case and will be compared to the other ones. Moreover, a variation of the base case is presented as well in which only offshore sequestration is employed.

4.1.1 A.ECO.50%

This is the base case, with the numeric results reported in Table 4.1, an explanation of the variables, parameters and functions related to them will be provided to understand the solution.

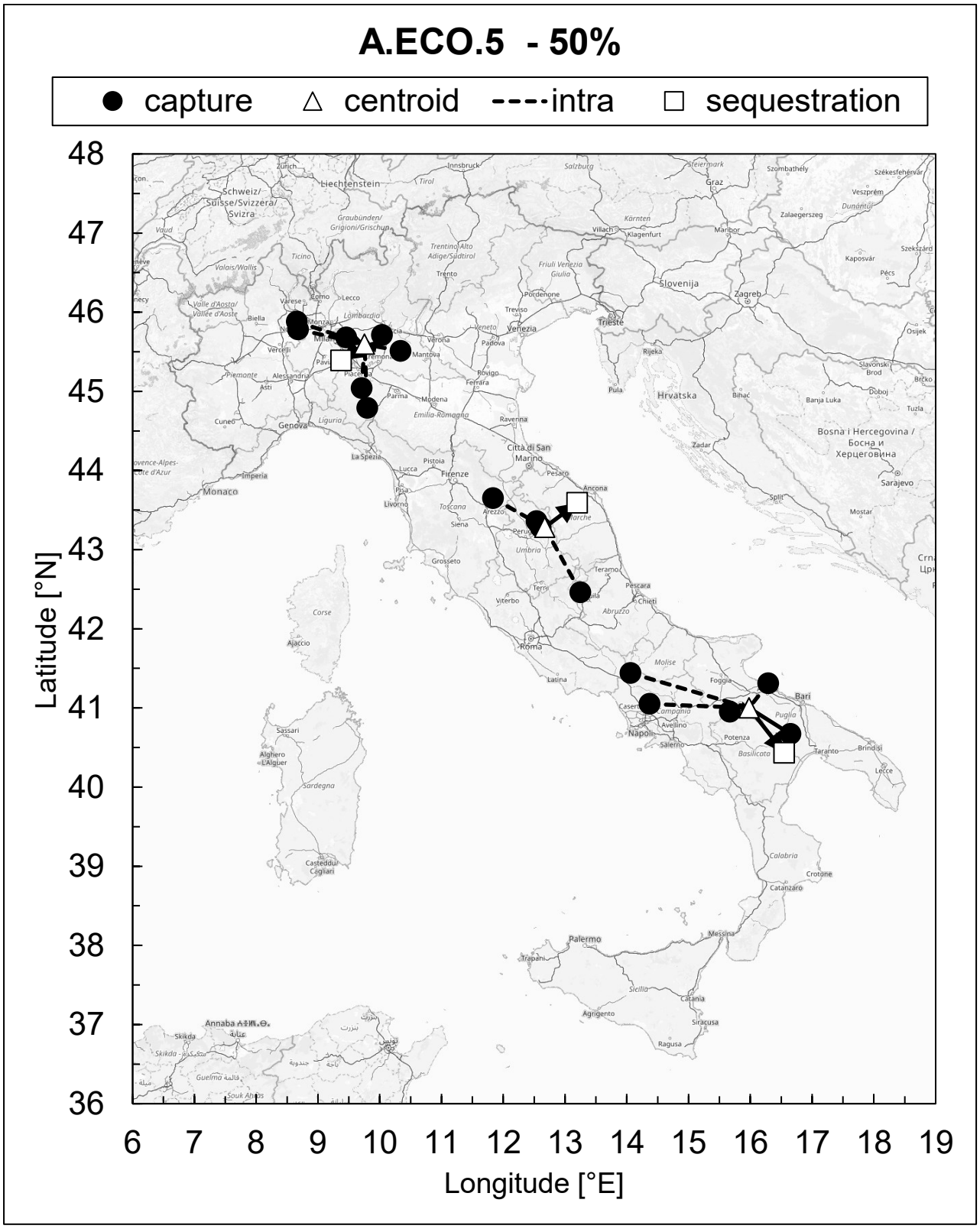
Table 4.1 – *Costs and emissions of all A.ECO.50% subcases optimisation in terms of: total costs TC [B€], capture cost TCC [B€], transport cost TTC [B€], sequestration cost TSC [B€] and their relative specific cost [€/t] expressed to the amount in tons [t] of overall sequestrated CO_2. The final net emission E [Mt], initial E^0 [Mt], additional ΔE [Mt], sequestrated E^{out} [Mt] and related to pumping $E^{p,tot}$ [Mt].*

Subcase	***TC***		***TCC***		***TTC***		***TSC***		***E***	E^0	ΔE	E^{out}	$E^{p,tot}$
	[B€]	[€/t]	[B€]	[€/t]	[B€]	[€/t]	[B€]	[€/t]	[Mt]	[Mt]	[Mt]	[Mt]	[Mt]
A.ECO.5	8.64	65.3	6.93	52.4	0.755	5.70	0.952	7.20	119	238	12.9	132	0.089
A.ECO.8	8.53	64.5	6.93	52.4	0.653	4.94	0.952	7.20	119	238	12.9	132	0.078
A.ECO.10	8.55	64.7	6.93	52.4	0.672	5.08	0.952	7.20	119	238	12.9	132	0.081

From the three subcases of Scenario A, the cost required for the SC is for A.ECO.5 of 8.64 B€ which correspond to 65.4 €/t, while for A.ECO.8 *TC* is equal to 8.53 B€, with a specific cost of 64.5 €/t, and lastly A.ECO.10 with 8.55 B€ with 64.7 €/t. Comparing these values, A.ECO.8 has the lowest one among them. However, looking at the costs of the three stages, there are some considerations to do. For the capture stage, *TCC* is always equal to 6.93 B€ in every subcase. This is caused by the fact the model selects the same capture technology to apply for all nodes in each subcase, and as a matter of fact, the specific cost of 52.4 €/t is that of the cost of the Calcium Looping (CaL) technology (*link to chapter 2).* Because of this *E,* ΔE and E^{out} give the same result, since all these variables depends on $E_{k,n,t}^{in,CAPT}$, which depends in turn from the capture technology *k* in Eq. (3.8). Similarly, the specific cost [€/t] for sequestration is equal to USC (Section 3.5.1) (i.e.; 7.20 €/t), meaning that only onshore sequestration is employed and that in Eq. (3.28) off_c is always equal to 1. Only the cost and emission related to the transport stage are different in each subcase, because transport heavily depends on the clustering (Section 3.4). Therefore, the main differences among the subcases of Scenario A are constituted by the results emerging from the optimisation of the transport stage, in which using 8 clusters gives a

lower *TTC* and even $E^{p,tot}$ (i.e., 0653 B€ and 4.94 €/t). As for the results in terms of costs shares, and as average among the three subcases, *TCC* constitutes 81% of *TC*, while *TSC* only an 11% and the remaining 8% is from *TTC.*

All the subcases are represented with individual maps to show how the SC infrastructure would be in Figure 4.1(A.ECO.5), Figure 4.2 (A.ECO.8) and in Figure 4.3 (A.ECO.10). As expected from the numeric results, there is no offshore sequestration. Moreover, there is no capture in Sardinia and Sicily islands, since the infrastructure is built onshore. In particular, in all of the three subcases, the cluster in the northern region of Lombardia, in the middle region of Umbria and in the southern region of Puglia are always selected, however, the main differences in the selection of nodes, centroids and sequestration nodes are mostly located in the middle and southern regions of Umbria, Lazio, Campania, Basilicata and Puglia. This outcome is justified by the fact that using a higher number *k* of centroids (Section 3.4) mostly affects the clusters in the middle and southern regions. In fact it is possible to understand why the transport costs of A.ECO.5 are higher compared to the other subcases. With less centroids, one cluster has more nodes, and some have a long distance from the centroid. Because of this, the centroids in between the regions of Umbria and Marche, and between Basilicata and Puglia, receive flowrates of capture CO_2 from far nodes (i.e.; the dashed line in the figures) and a longer distance increases the intra-connection cost given from Eq. (3.16). Moreover, even three sequestration basins are always selected: Lombardia 1, Marche 1 and Bradanica (in the region of Basilicata; Table 3.3). The model will select the sequestration nodes that allow to reduce to a minimum $E^{p,tot}$, or in other words the nodes that are nearer to the centroid. This means that the centroids in Lombardia, Umbria and Puglia, do not change significantly their position to make the model selecting another sequestration basin for them.



igure 4.1 – *CCS SC infrastructure for A.ECO.5 with α = 50%.*

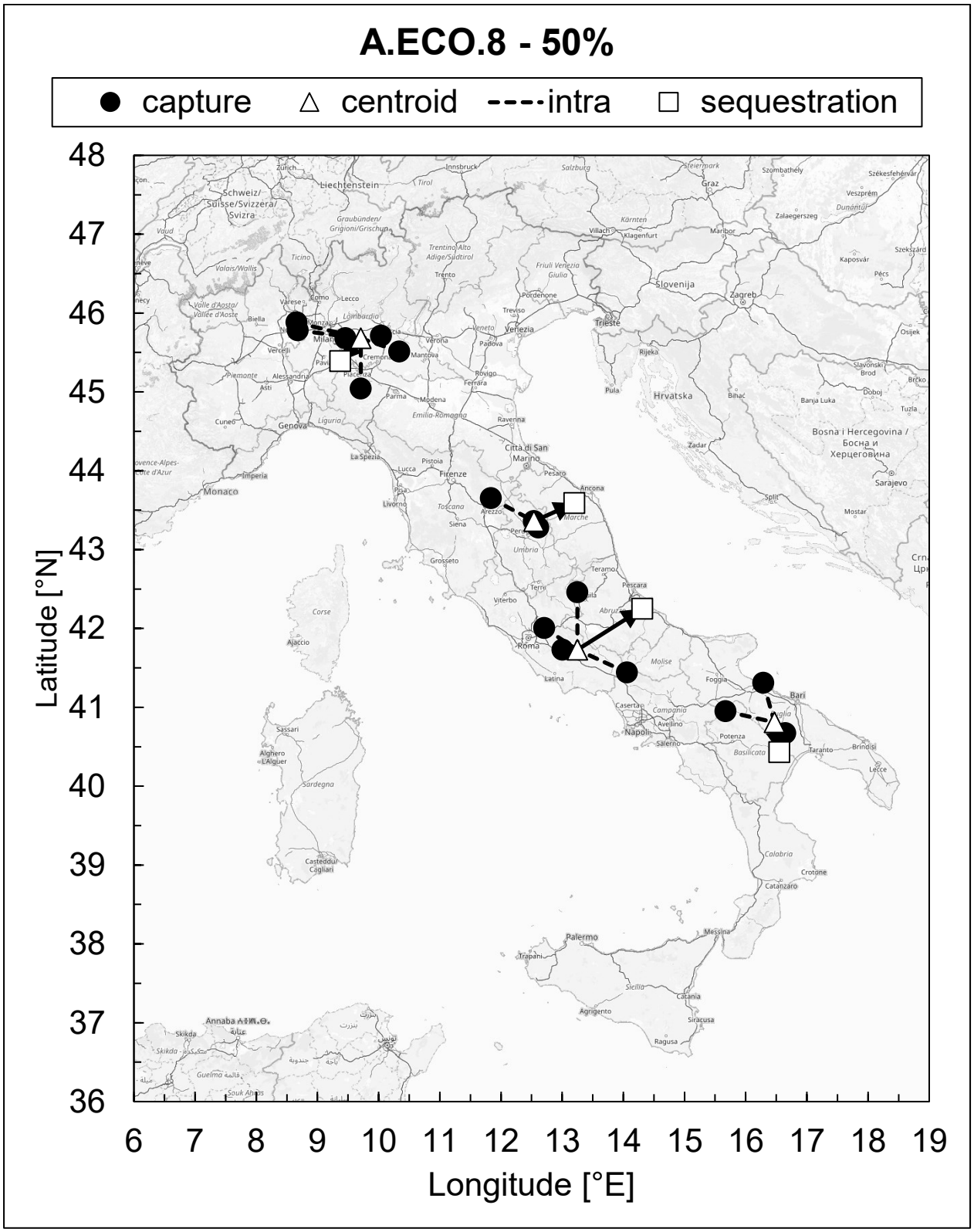


Figure 4.2 – *CCS SC infrastructure for A.ECO.8 with α = 50%.*

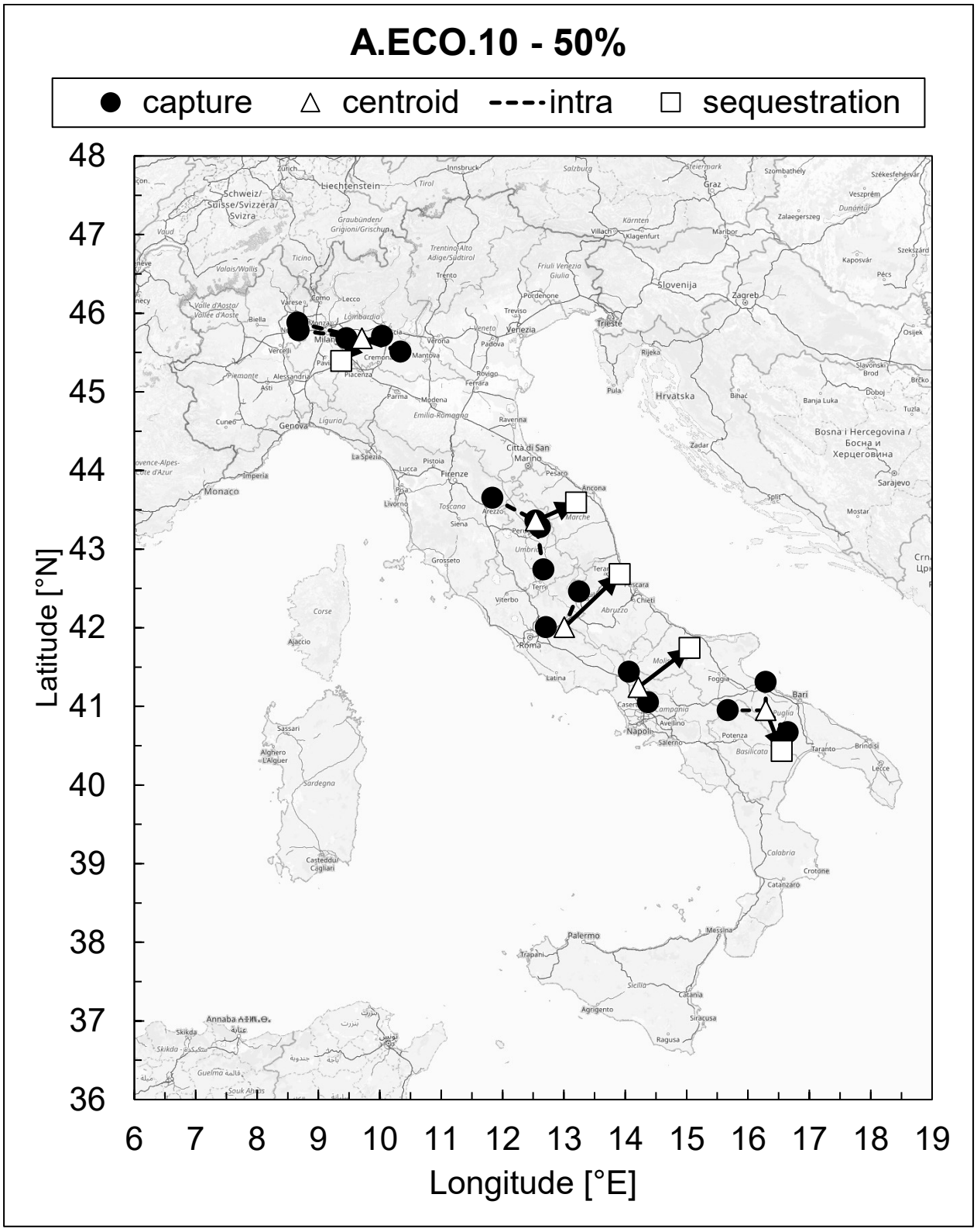


Figure 4.3 – *CCS SC infrastructure for A.ECO.10 with α = 50%.*

4.1.2 B.ECO.50%

This is the ECO case for Scenario B, in which the additional emissions of the capture system are now based on the carbon intensity of renewable-based energy mix (*link to chapter 2).* For this case, the same carbon target reduction of the base case of 50% is considered. In Table 4.2 the numeric results are reported.

Table 4.2 – *Costs and emissions of all B.ECO.50% subcases optimisation in terms of: total costs TC [B€], capture cost TCC [B€], transport cost TTC [B€], sequestration cost TSC [B€] and their relative specific cost [€/t] expressed to the amount in tons [t] of overall sequestrated CO_2. The final net emission E [Mt], initial E^0 [Mt], additional ΔE [Mt], sequestrated E^{out} [Mt] and related to pumping $E^{p,tot}$ [Mt].*

Subcase	***TC***		***TCC***		***TTC***		***TSC***		***E***	E^0	**Δ*E***	E^{out}	$E^{p,tot}$
	[B€]	[€/t]	[B€]	[€/t]	[B€]	[€/t]	[B€]	[€/t]	[Mt]	[Mt]	[Mt]	[Mt]	[Mt]
B.ECO.5	8.36	65.0	6.73	52.4	0.699	5.43	0.926	7.20	119	238	9.38	128	0.085
B.ECO.8	8.28	64.3	6.73	52.4	0.615	4.78	0.926	7.20	119	238	9.38	128	0.077
B.ECO.10	8.31	64.7	6.73	52.4	0.649	5.05	0.926	7.20	119	238	9.38	128	0.076

There is no difference in the options selected (i.e.; capture technology, onshore or offshore sequestration) in Scenario B by the introduction of a renewable energy mix in the accounting of carbon intensity for the determination of indirect emissions deriving from capture. In fact, the specific cost of *TCC* is always equal to 52.4 €/t for each subcase, and the specific cost for *TSC* is equal to 7.20 €/t, meaning that the model always employs the CaL technology and an onshore sequestration. However, the costs and the emissions are lower compared to the base case in Scenario A. This can be explained comparing the additional emissions, which are equal to 9.38 Mt , while for Scenario A they are equal to 12.9 Mt. Using a renewable energy mix lowered the additional emissions from operating the CaL technology *(link chapter 2)*. Because of this decrease, to obtain a carbon reduction target of 50% the model needs to capture less CO_2 from the nodes, which results in a lower E^{out} equal to 128 Mt instead of 132 Mt as in Scenario A. Of course, with less CO_2 to sequestrate, a lower *TSC* equal to 0.926 B€ is obtained. Moreover, the SC infrastructures of the subcase are the same as in the base case, and thus lower transport costs are determined by lower transported flowrates in Scenario B compared to Scenario A. Overall, the use

of a renewable energy mix allows to decrease the costs, more specifically comparing the best subcase from each Scenario, from 8.53 B€ with a specific cost of 64.5 €/t (i.e.; A.ECO.8) to 8.28 B€ with 64.3 €/t. A decrease of 0.2 €/t saves 0.25 B€.
For the economic optimisation of Scenario B there is no SC configuration representation since it would just be a copy of Scenario A.

4.1.3 Sensitivity analysis on α

The sensitivity analysis results are reported in Table 4.3.

Table 4.3 - *Costs and emissions of the sensitivity analysis α on the A.ECO case in terms of: total costs TC [B€], capture cost TCC [B€], transport cost TTC [B€], sequestration cost TSC [B€] and their relative specific cost [€/t] expressed to the amount in tons [t] of overall sequestrated CO_2. The final net emission E [Mt], initial E^0 [Mt], additional ΔE [Mt], sequestrated E^{out} [Mt] and related to pumping $E^{p,tot}$ [Mt].*

Subcase	α	***TC***		***TCC***		***TTC***		***TSC***		E	E^0	ΔE	E^{out}	$E^{p,tot}$
	[%]	[B€]	[€/t]	[B€]	[€/t]	[B€]	[€/t]	[B€]	[€/t]	[Mt]	[Mt]	[Mt]	[Mt]	[Mt]
A.ECO.5.	30	5.04	63.6	4.15	52.4	0.316	3.99	0.571	7.20	167	238	7.79	79.2	0.041
A.ECO.5	50	8.64	65.3	6.93	52.4	0.755	5.70	0.952	7.20	119	238	12.9	132	0.089
A.ECO.5	70	12.5	67.4	9.71	52.4	1.45	7.86	1.33	7.20	71.1	238	18.2	185	0.166
A.ECO.8	30	5.02	63.3	4.15	52.4	0.294	3.70	0.571	7.20	167	238	7.79	79.2	0.037
A.ECO.8	50	8.53	64.5	6.93	52.4	0.653	4.94	0.952	7.20	119	238	12.9	132	0.078
A.ECO.8	70	12.2	65.9	9.71	52.4	1.18	6.37	1.33	7.20	71.1	238	18.2	185	0.136
A.ECO.10	30	5.03	63.4	4.15	52.4	0.307	3.87	0.571	7.20	167	238	7.79	79.2	0.039
A.ECO.10	50	8.55	64.7	6.93	52.4	0.672	5.08	0.952	7.20	119	238	12.9	132	0.081
A.ECO.10	70	12.2	66.0	9.71	52.4	1.19	6.44	1.33	7.20	71.1	238	18.2	185	0.127

For the capture stage, the specific cost of *TCC* is always equal to 52.4 €, while for the sequestration stage is equal to 7.20 €/t. This means that the model still selects the CaL technology for capture and an onshore sequestration independently from the value of α. In terms of costs optimisation, the subcase with 8 clusters is always the one with the lowest *TC* due to a better optimisation of the

transport stage. Although, when compared to A.ECO.10 with α equal to 30% and 70%, the difference between the specific costs is only just 0.1 €/t while with the base case is 0.2 €/t. This difference is given from the transport stage costs and this means that for high or low values of α, *TC* is less affected by the number of clusters (i.e., 8 and 10 clusters) and that the transport costs entail just marginal difference between the two subcases. But, with the emissions related to the transport, there is an interesting result. For α equal to 30% and 50%, A.ECO.8 has always the lowest $E^{p,tot}$ respectively equal to 0.037 Mt and 0.078 Mt, among the subcases, while for α equal to 70%, A.ECO.10 has the lowest $E^{p,tot}$ equal to 0.127 Mt versus the 0.136 Mt of A.ECO.8 . This can be explained by the fact that to achieve a reduction of 70%, the capture is operated in more nodes, and since with a higher number of clusters the intra distances between nodes and centroid decrease, Eq. (3.21) provides a lower result that will give as a consequence a lower value of $E_t^{pump,tot}$ from Eq. (3.22). About the subcase with 5 clusters, overall, it is always the one with the highest costs and emissions related to transport. On average, for the case with a reduction of 30%, the specific *TC* is 0.2 €/t higher compared to the other subcases, for a reduction of 50% is 0.7 €/t higher and for a reduction of 70% is 1.4 €/t more expensive. This means that dealing with higher volumes of captured CO_2 and using nodes that are farther and farther from the centroids, the transport costs increase a lot, and in fact for the case with α equal to 70%, A.ECO.5 has a *TTC* of 1.45 B€, versus a *TTC* of 1.18 B€ for A.ECO.8 and a *TTC* of 1.19 B€ for A.ECO.10

Regarding the SC configuration, the following subcases will be represented: A.ECO.8 - 30% in Figure 4.4, A.ECO.8 - 70% in Figure 4.5 and A.ECO.10 -70% in Figure 4.6. Starting with Figure 4.4, then Figure 4.2 (A.ECO.8 50%), and lastly Figure 4.5 it is possible to observe how the SC infrastructure develops with the increasing of the carbon reduction target. In Figure 4.4 three centroids are selected in the regions of Lombardia, Umbria and Puglia. Increasing the carbon reduction to 50%, in Figure 4.2, it is evident that the capture is operated in more nodes and in another cluster with the centroid in Lazio. Because of this the transport costs are equal to 0.653 B€ versus the 0.294 B€ of the previous case. This means that the additional sequestration of 52.8 Mt between the two cases increase of 2.2 times *TTC.* In figure 4.5 the infrastructure becomes more complex, however, from each centroid there is only one connection (i.e.; only one flowrate) with the corresponding sequestration node. This means that the sequestration nodes are able to storage all the CO_2 captured after a time span of 20 years. In Figure 4.6 it is possible to observe how in

A.ECO.10 – 70% the emissions related to the transport are lower than in A.ECO.8 – 70%, the intra connections are shorter (i.e.; the dashed lines). Moreover, a very interesting result is that from the centroid in Lombardia, the captured CO_2 is sent into two different sequestration nodes, and the reason is because one of the two nodes reached its maximum capacity. The two nodes are Lombardia 1 and Lombardia 2 from Table 3.2 with the former near to Piemonte, the latter near to Veneto. Lombardia 1 has a storage capacity of 76 Mt, and in that node a total of 74.7 Mt of CO_2 is sequestrated in 20 years (Table 4.4). This is important because it happens in the economic case with α equal to 70%, which has a lower reduction target than the ENV cases.

Table 4.4 – Sequestration nodes, capacity [Mt], sequestrated CO_2 in 1 year [Mt] and final CO_2 sequestrated after 20 years [Mt] for A.ECO.10 – 70%.

Node	**Name**	**Storage capacity**	**Yearly sequestrated amount**	**Final sequestrated amount**
		[Mt]	[Mt]	[Mt]
C101	Lombardia 1	76	3.73	74.7
C102	Lombardia 2	356	0.97	19.4
C105	Marche 1	716	1.68	33.6
C106	Abruzzi 1	46	0.93	18
C111	Molise 2	140	0.77	15.4
C112	Bradanica	688	1.15	23

From Table 4.4 only Lombardia 1 is near to be saturated, missing only 1.3 Mt to reach the limit. However, all the other nodes are far from reaching their total storage capacity. The case of saturation for Lombardia 1 can explained for its position. The model will try to minimize the emissions related to transport selecting the shortest distance, and Lombardia 1 is the nearest node to the centroids in Piemonte and Lombardia. But, since the model cannot sequestrate over the storage capacity, it is forced to split the flowrate within the two basins located in Lombardia.

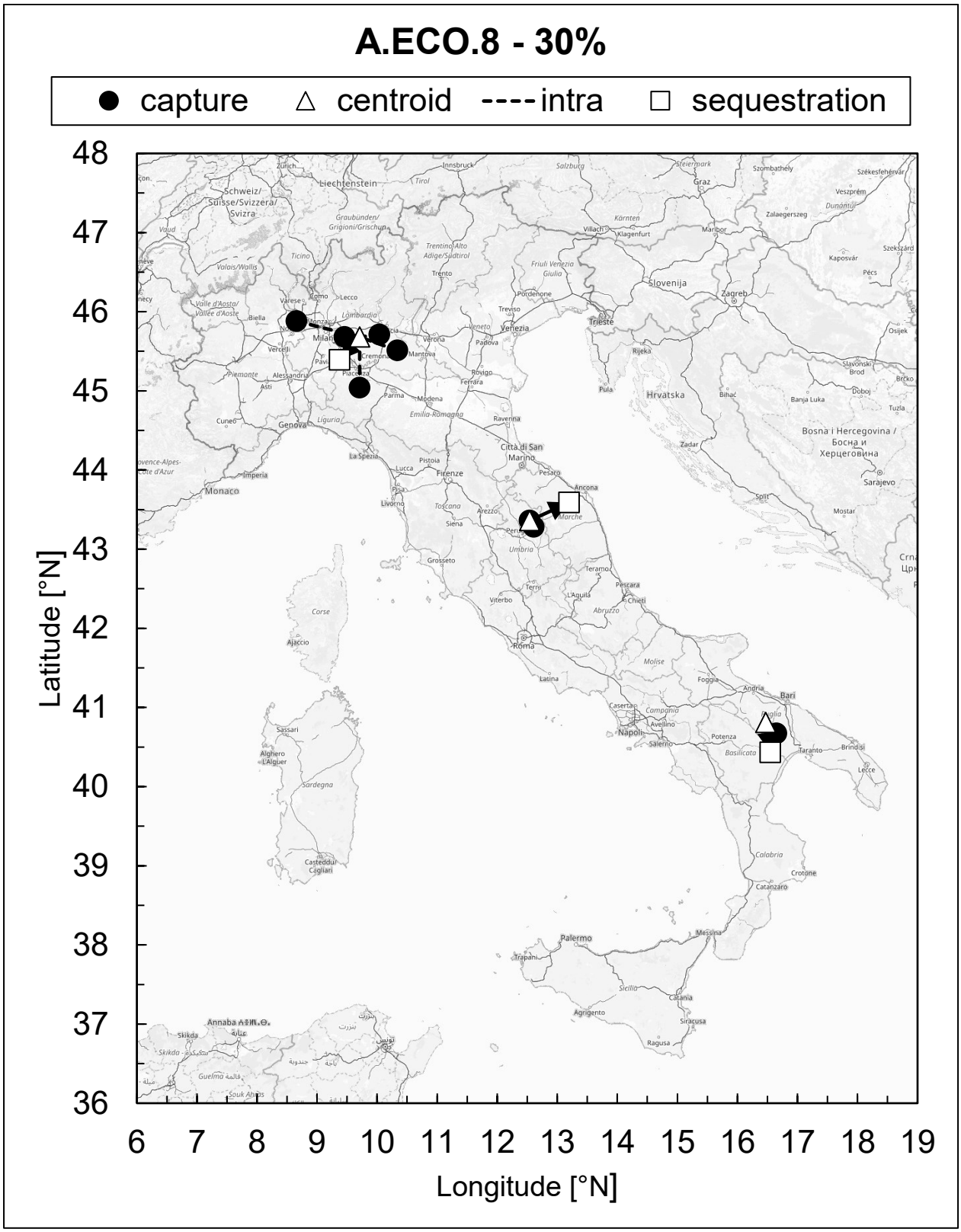


Figure 4.4 – *CCS SC infrastructure for A.ECO.8 with α = 30%.*

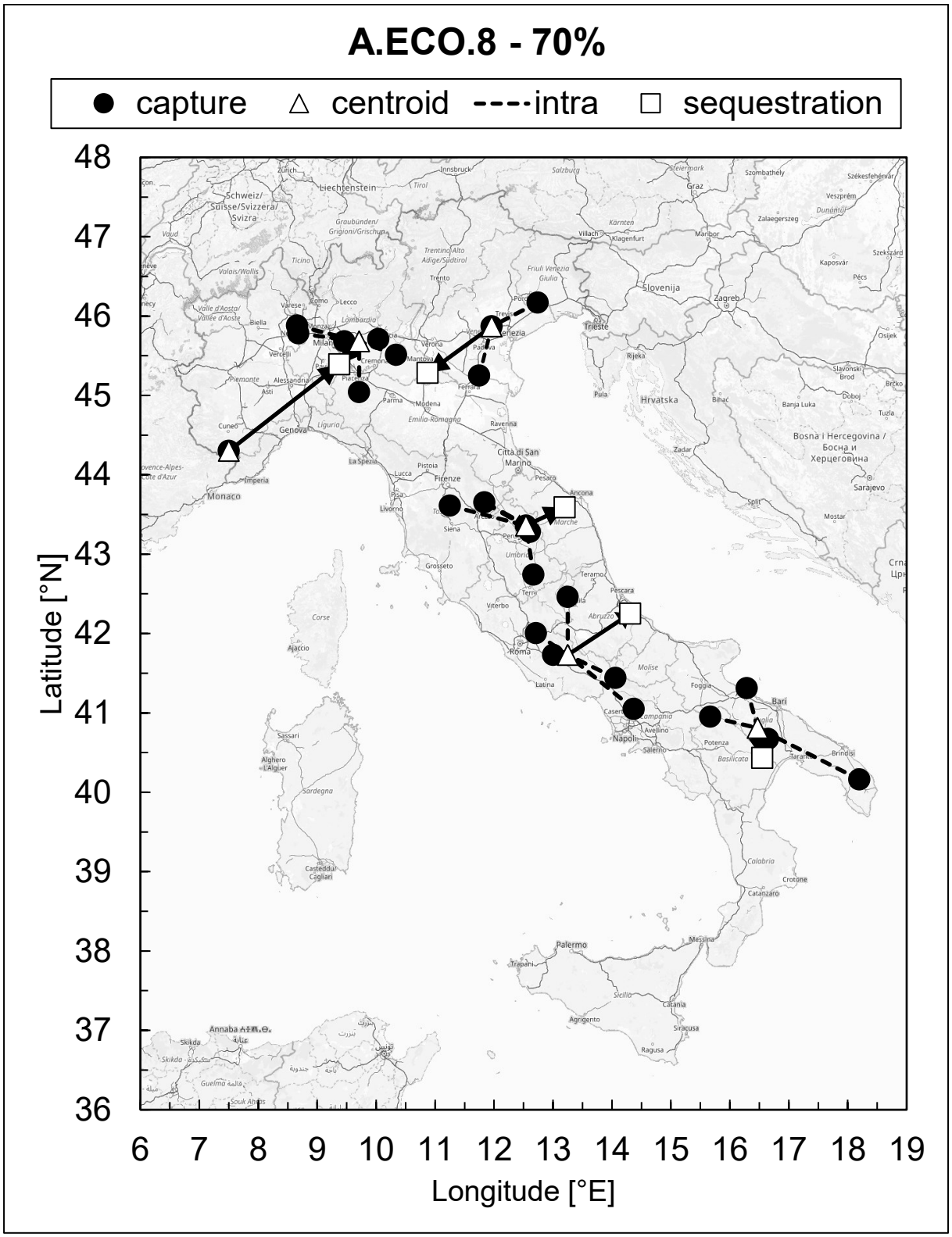


Figure 4.5 – *CCS SC infrastructure for A.ECO.8 with α = 70%.*

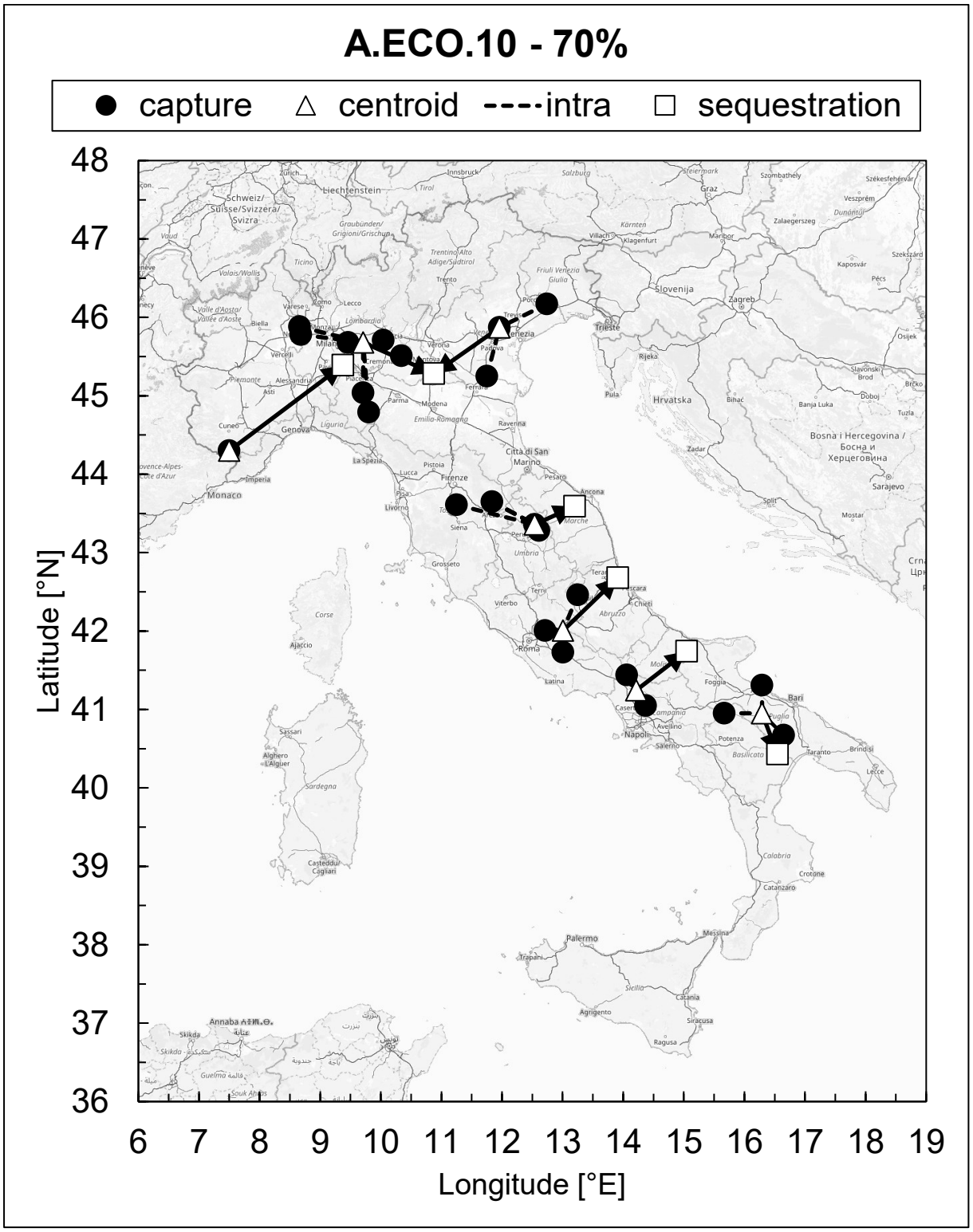


Figure 4.8 – *CCS SC infrastructure for A.ECO.10 with α = 70%.*

4.1.4 Comparison between onshore and only offshore sequestration

In this section a variation of the base case is presented and compared with it. In this new case study it is considered only an offshore sequestration. This is implemented in the model forcing that all the inter connections with onshore sequestration nodes are nulls and only offshore sequestration nodes are considered. As a consequence in Eq. (3.28) off_c is always equal to 2.5.

Table 4.5 – *Costs and emissions of base case and A.ECO with only offshore sequestration subcases optimisation in terms of: total costs TC [B€], capture cost TCC [B€], transport cost TTC [B€], sequestration cost TSC [B€] and their relative specific cost [€/t] expressed to the amount in tons [t] of overall sequestrated CO_2. The final net emission E [Mt], initial E^0 [Mt], additional ΔE [Mt], sequestrated E^{out} [Mt] and related to pumping $E^{p,tot}$ [Mt]. The names with * refers to the offshore case.*

Subcase	*TC*		*TCC*		*TTC*		*TSC*		*E*	E^0	ΔE	E^{out}	$E^{p,tot}$
	[B€]	[€/t]	[B€]	[€/t]	[B€]	[€/t]	[B€]	[€/t]	[Mt]	[Mt]	[Mt]	[Mt]	[Mt]
A.ECO.5	8.64	65.3	6.93	52.4	0.755	5.70	0.952	7.20	119	238	12.9	132	0.089
*A.ECO.5**	10.9	82.8	6.93	52.4	1.64	12.4	2.38	18.0	119	238	12.9	132	0.221
A.ECO.8	8.53	64.5	6.93	52.4	0.653	4.94	0.952	7.20	119	238	12.9	132	0.078
*A.ECO.8**	10.7	81.4	6.93	52.4	1.45	10.9	2.38	18.0	119	238	12.9	132	0.206
A.ECO.10	8.55	64.7	6.93	52.4	0.672	5.08	0.952	7.20	119	238	12.9	132	0.081
*A.ECO.10**	11.1	84.2	6.93	52.4	1.82	13.8	2.38	18.0	119	238	12.9	132	0.207

Table 4.5 reports the results from the base case, which has only onshore sequestration, and the case with only offshore sequestration. The first difference is in *TSC*, from 7.20 €/t of the onshore sequestration to 18.0 €/t of the offshore sequestration. For the capture stage, *TTC* is always equal to 6.93 B€ with the specific cost of 52.4 €/t the same as the CaL technology cost. On the other hand, *TTC* increases greatly with $E^{p,tot}$. In fact, from a maximum of 0.089 Mt from A.ECO.5, $E^{p,tot}$ raised to 0.221 Mt for the same subcase, an increase of 148% from base case. For *TTC*, A.ECO.8* is the subcase with the lowest result equal to 1.45 B€ (i.e., 10.9 €/t), but it is more than 0.797 B€ from A.ECO.8. The other two subcases have a higher *TTC* equal to 1.64 B€, corresponding to 12.4 €/t for the subcase with 5 clusters, and equal to 1.82 B€ with 13.8 €/t for the

subcase with 10 clusters. In this case, using 10 clusters than 5 results in a higher *TTC* and a higher *TC* too. In fact, A.ECO.10* has a specific *TC* of 84.2 €/t, while A.ECO.5* of 82.8 €/t, that is 1.4 €/t as a difference.

To understand these differences, the SC configurations of the subcases need to be analysed. In Figure 4.9 the infrastructure of A.ECO.5* is represented, and the first difference from A.ECO.8* (Figure 4.10) and A.ECO.10* (4.11) is that the sequestration is done in only two nodes, Emilia Mare and Abruzzi Mare. It considers only 3 clusters, in Lombardia, Umbria and Puglia and it is visible there are at least 5 nodes for each cluster. In Figure 4.10 and Figure 4.11 the centroids in Lombardia and Umbria are the same as in Figure 4.9, however, in these two subcases the rest of the capture is done, for A.ECO.8*, in the clusters of Lazio and Puglia, and for A.ECO.10* in Lazio, Campania and Puglia. The higher transport costs in A.ECO.10* can be explained by the fact that the capture is operated in more clusters resulting then in more inter connections, and since the number of nodes belonging to a cluster decreases, this means usually a lower flowrate, which has a higher cost. With lower flowrates and more inter connections that are all offshore transports, thus more expensive (Table 3.3), the subcases with 10 clusters gives a worse *TTC* than A.ECO.5*.

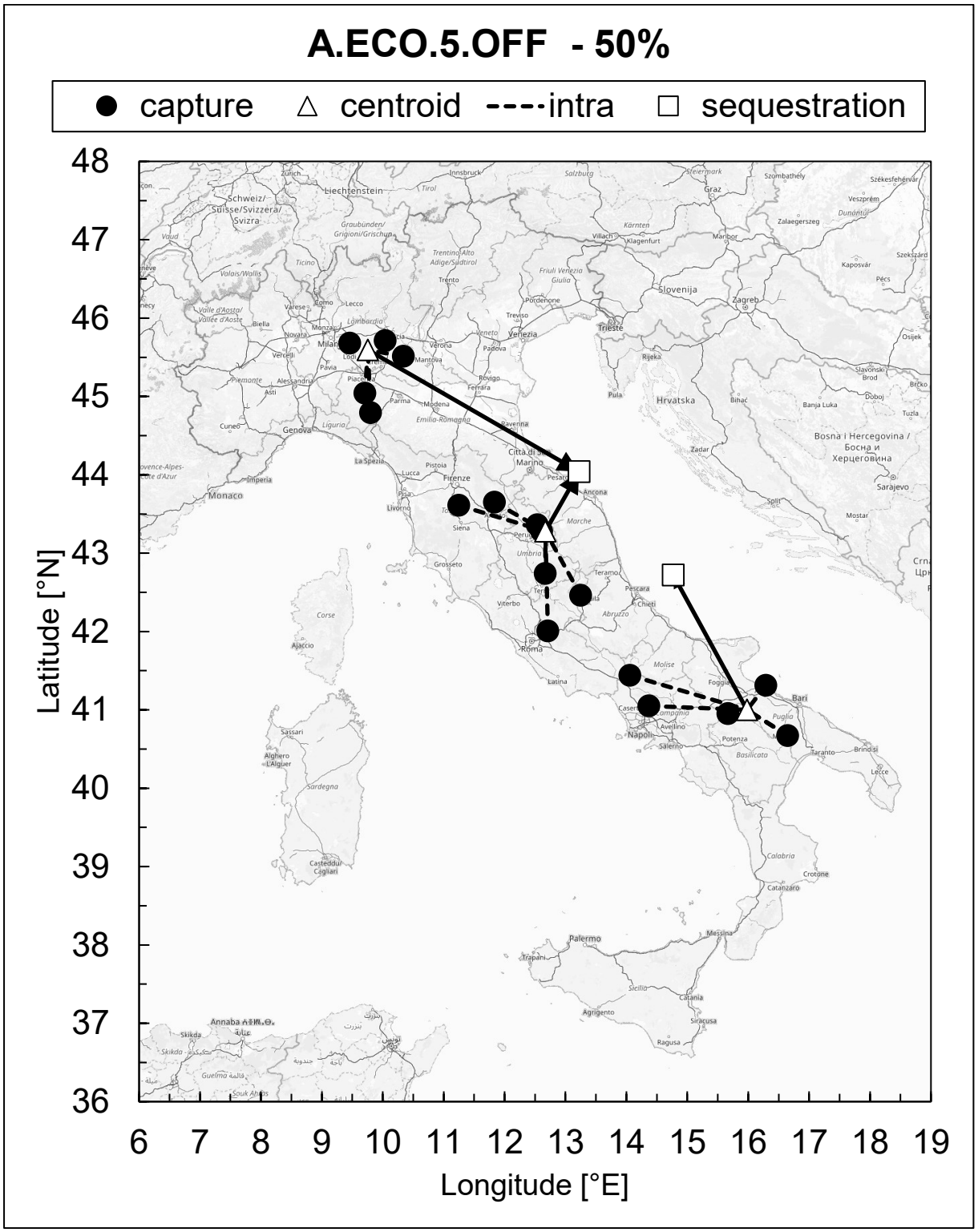


Figure 4.9 – *CCS SC infrastructure for A.ECO.5 with α = 50% and only offshore sequestration.*

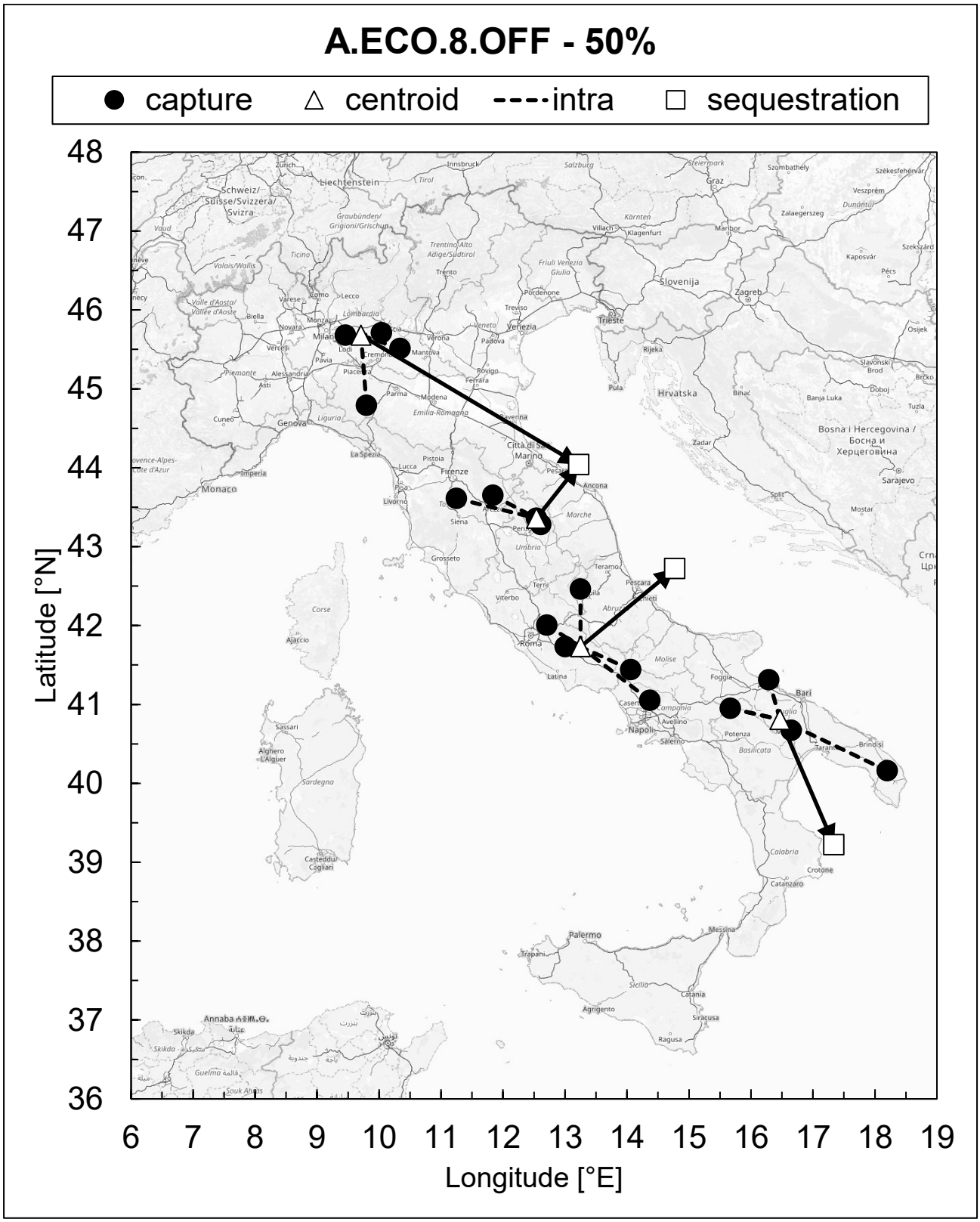


Figure 4.10 – *CCS SC infrastructure for A.ECO.8 with α = 50% and only offshore sequestration*

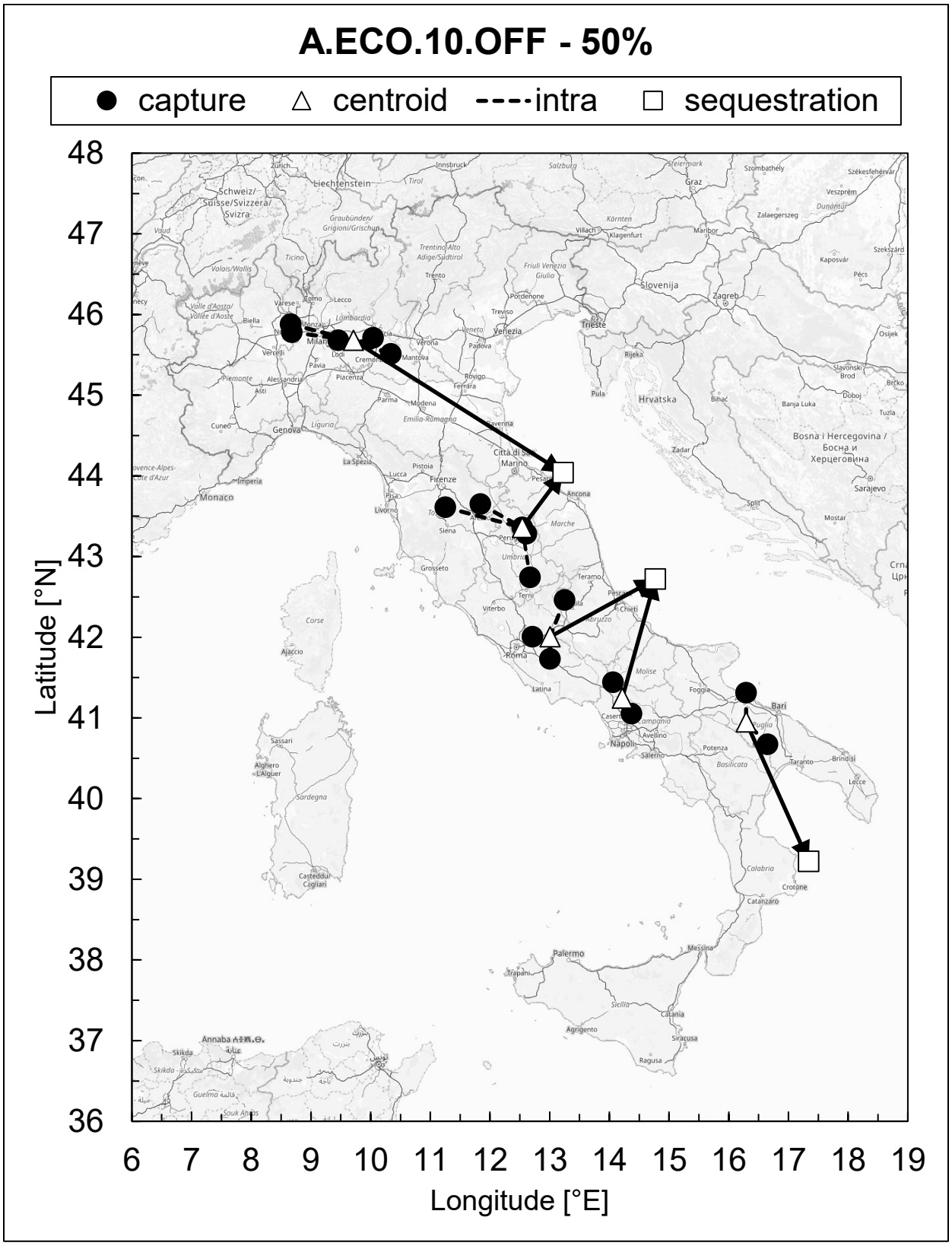


Figure 4.11 – *CCS SC infrastructure for A.ECO.10 with α = 50% and only offshore sequestration.*

4.2 Environmental optimisations

For the environmental optimisation, the model aims to minimise *E* given by Eq. (3.6). For this case, there is no need to set a value for α as done for the ECO cases, because Eq. (3.29) will be independent now from α and its value can never be equal or greater than 1.

4.2.1 A.ENV

This is the ENV case for Scenario A. Table 4.6 contains the quantitative results and the SC design of each subcase is given in Figure 4.13, Figure 4.14 and Figure 4.15.

Table 4.6 – *Costs and emissions of all A.ENV subcases optimisation in terms of: total costs TC [B€], capture cost TCC [B€], transport cost TTC [B€], sequestration cost TSC [B€] and their relative specific cost [€/t] expressed to the amount in tons [t] of overall sequestrated CO_2. The final net emission E [Mt], initial E^0 [Mt], additional ΔE [Mt], sequestrated E^{out} [Mt] and related to pumping $E^{p,tot}$ [Mt].*

Subcase	***TC***		***TCC***		***TTC***		***TSC***		***E***	E^0	ΔE	E^{out}	$E^{p,tot}$
	[B€]	[€/t]	[B€]	[€/t]	[B€]	[€/t]	[B€]	[€/t]	[Mt]	[Mt]	[Mt]	[Mt]	[Mt]
A.ENV.5	15.1	69.8	11.3	52.4	2.22	10.2	1.56	7.20	42.9	238	21.3	217	0.222
A.ENV.8	14.7	67.8	11.3	52.4	1.78	8.22	1.56	7.20	42.9	238	21.3	217	0.187
A.ENV.10	14.8	68.3	11.3	52.4	1.85	8.54	1.60	7.39	42.9	238	21.3	217	0.177

With the results obtained, it is possible to calculate the value of the carbon reduction, which is equal to 81% for every subcase. If the additional emissions were equal to 0, the reduction would have been of 91% which is equal to *CCR* of the CaL technology (*link to chapter 2*). In fact the specific cost is 52.4 €/t, and this means that even for the environmental optimisation, this technology is the best one for Scenario A. Because of this, *TCC* and the emissions are the same for each subcase and as for the base case, only the transport stage has different results. Thus, comparing $E^{p,tot}$ the best environmental optimisation is achieved in A.ENV.10 with 0.177 Mt and it has a *TC* of 14.8 B€, corresponding to 68.3 B€. A.ENV.8 has the lowest *TC* but its $E^{p,tot}$ is equal to 0.187 Mt. Moreover, A.ENV.10 entails the exploitation of an offshore basin and consequently in the latter

case study the value of *TSC* is higher than the other two, with a specific cost of 7.39 €/t instead of 7.20 €/t. In the sensitivity analysis of α, A.ECO.8 results always with the best optimization (i.e., lower *TC*) thus the subcase with 8 clusters from the ENV case will be used to compare *TC.* From A.ECO.8 with α equal to 50%, *TC* increases of 6.17 B€ (72%) and for the specific the difference is of 3.3 €/t, while it is of 2.6 B€ (20%) and 1.9 €/t from A.ECO.8 with a reduction of 70%.

The three subcases are represented in Figure 4.12 (A.ENV.5), Figure 4.13 (A.ECO.8) and Figure 4.14 (A.ENV.10). Since it is an environmental optimisation, the model captures the CO_2 from all the nodes in each subcase. The intra connections just show the full clusters (i.e.; centroid and all nodes belonging to it), while the inter connections are selected in terms of minimising the emissions due to transport. In A.ENV.10 there is an offshore sequestration located in South Italy, in the Ionian Sea (i.e. Calabria Ionica) from a cluster with a single node in Puglia. And this can be explained by the fact that the centroid is nearer to the offshore node than the onshore one. Another interesting result, already commented for A.ECO.10 – 70% (section 4.1.3) is the fact that in every subcase the sequestration node Lombardia 1 is always saturated (i.e.; 74.7 Mt for a limit of 76 Mt), however no other similar case is present in any of the subcases. In A.ENV.10 Abruzzi 1 is selected as sequestration node, but only 18 Mt are injected for a limit of 46 Mt (i.e., only 39% of the maximum capacity is reached after 20 years).

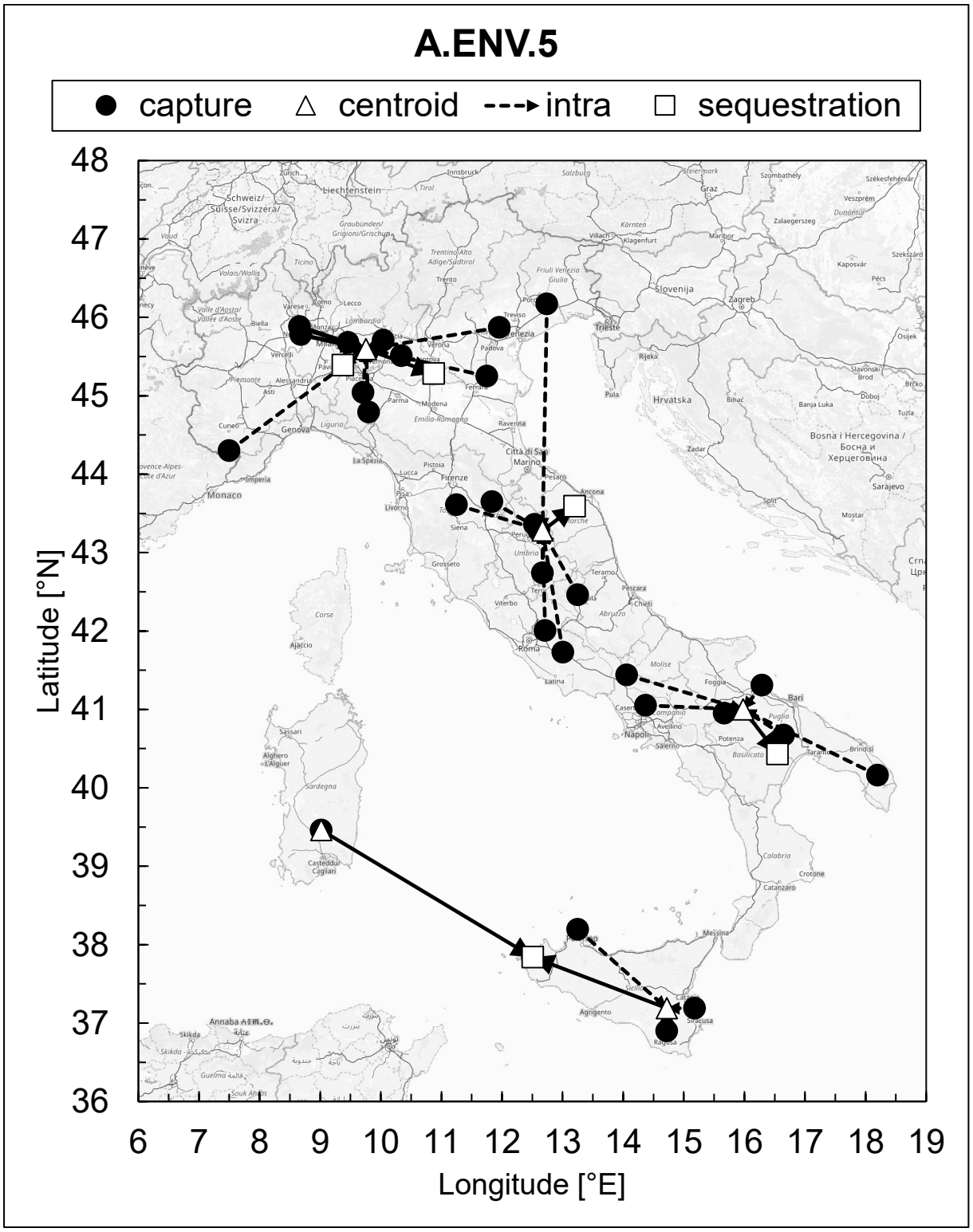


Figure 4.12 – *CCS SC infrastructure for A.ENV.5.*

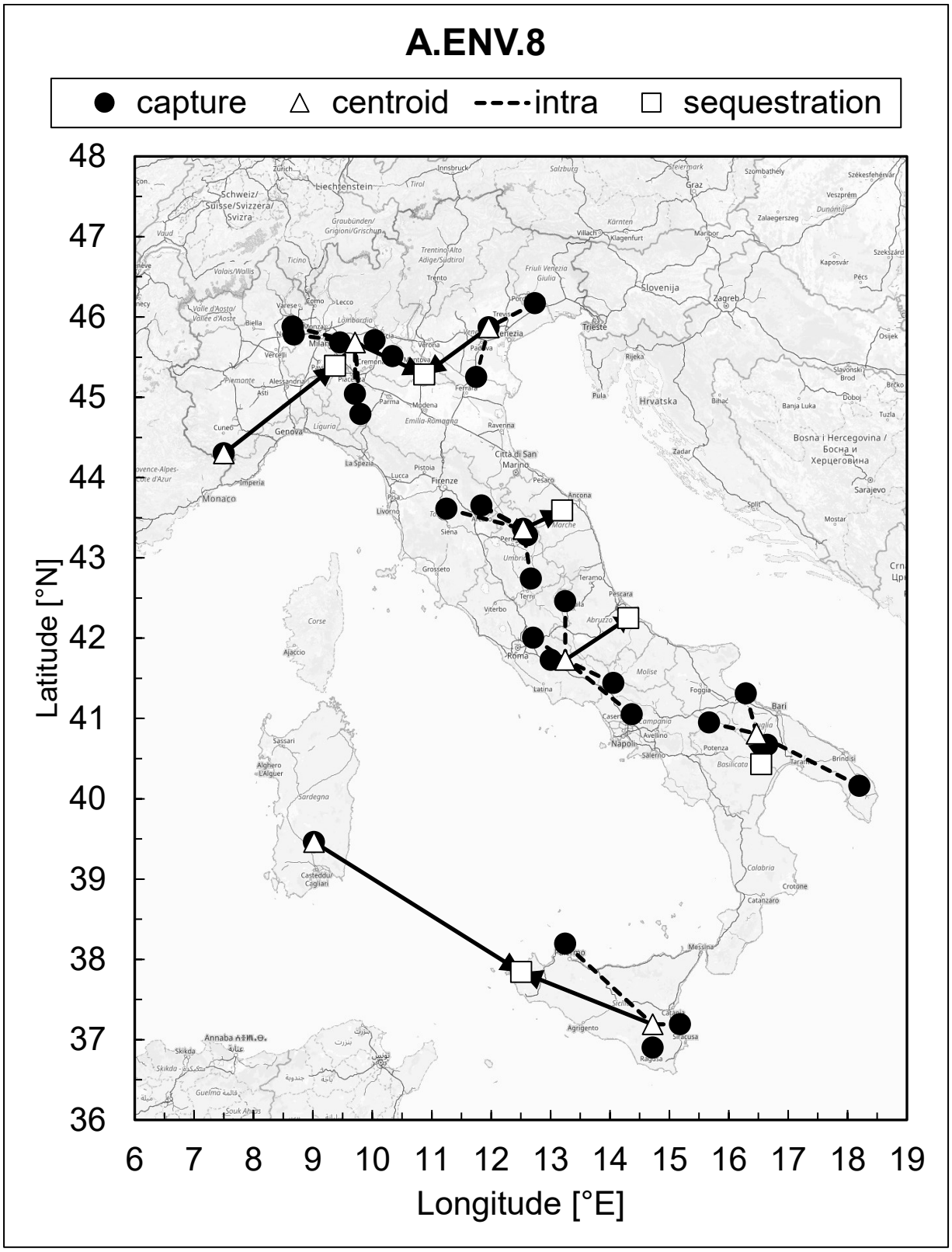


Figure 4.13 – *CCS SC infrastructure for A.ENV.8*

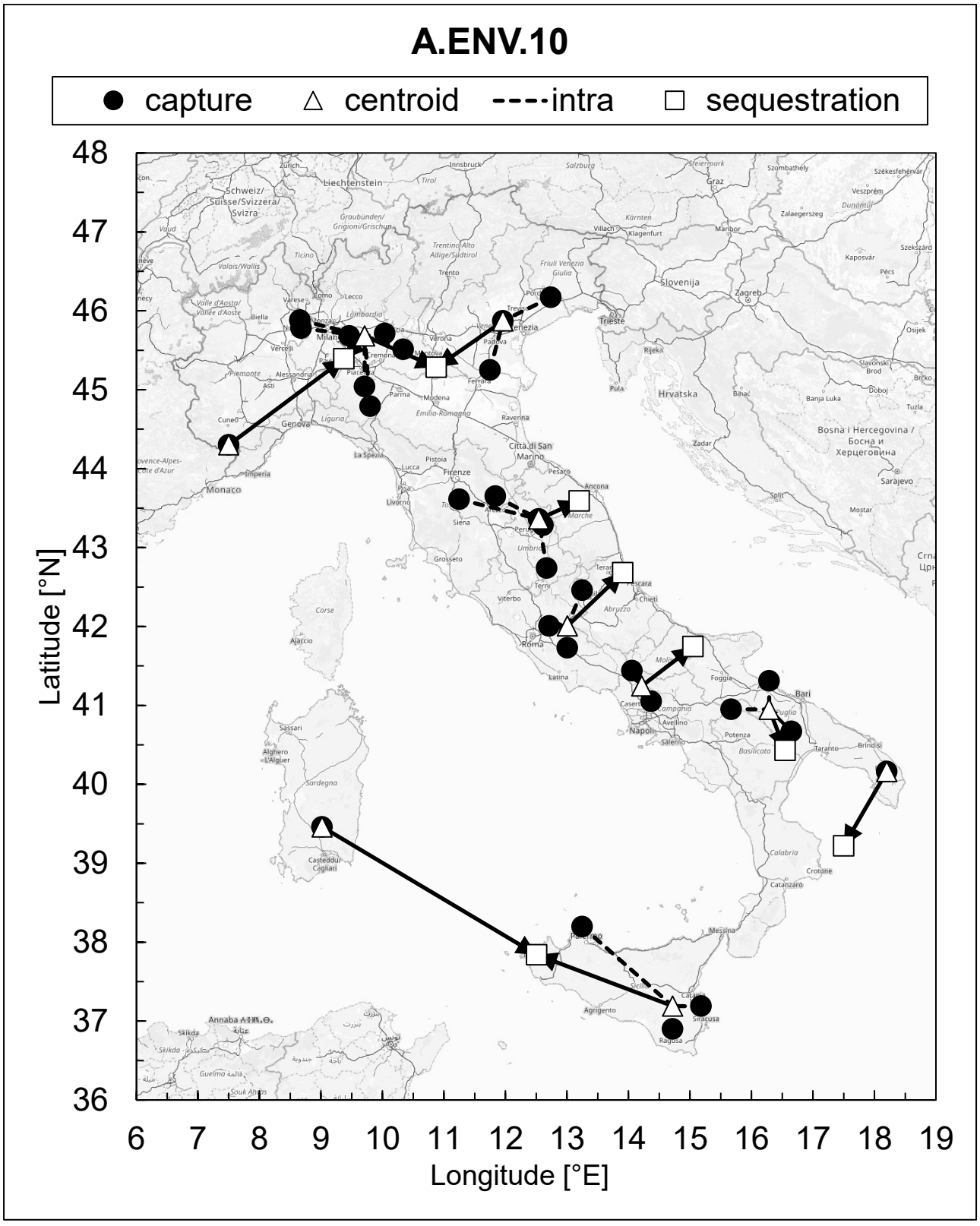


Figure 4.14 – *CCS SC infrastructure for A.ENV.10.*

4.2.2 B.ENV

As already explained in Section 4.1.2, in Scenario B the additional emissions due to the consumption of electricity are equal to 0. From the results reported in Table 4.7, overall, *TC* is higher than the A.ENV case of 6.5 B€.

Table 4.7 – *Costs and emissions of all B.ENV subcases optimisation in terms of: total costs TC [B€], capture cost TCC [B€], transport cost TTC [B€], sequestration cost TSC [B€] and their relative specific cost [€/t] expressed to the amount in tons [t] of overall sequestrated CO_2. The final net emission E [Mt], initial E^0 [Mt], additional ΔE [Mt], sequestrated E^{out} [Mt] and related to pumping $E^{p,tot}$ [Mt].*

Subcases	***TC***		***TCC***		***TTC***		***TSC***		***E***	E^0	ΔE	E^{out}	$E^{p,tot}$
	[B€]	[€/t]	[B€]	[€/t]	[B€]	[€/t]	[B€]	[€/t]	[Mt]	[Mt]	[Mt]	[Mt]	[Mt]
B.ENV.5	21.6	101	17.8	83.5	2.19	10.2	1.54	7.20	24.0	238	0.0	214	0.220
B.ENV.8	21.2	99.1	17.8	83.5	1.79	8.39	1.54	7.20	24.0	238	0.0	214	0.184
B.ENV.10	21.3	99.5	17.8	83.5	1.85	8.65	1.58	7.39	24.0	238	0.0	214	0.175

Looking at *TCC* there is an important difference from all the previous cases. The specific cost is equal to 83.5 €/t which is equal to the cost of the MAL capture system (*link to chapter 2)*. As a main consequence, the additional emissions are equal to 0 because the MAL technology only uses electrical power which is now provided from a renewable-energy mix source and this allows to obtain a carbon reduction of E^0 exactly the same as the *CCR* of the capture system, which is 90%. Regarding the sequestration, the same conclusions done for A.ENV are valid even for this case. For the transport, the infrastructure is exactly the same as in A.ENV case and because of this there is not a SC design of this case.

In the end, a whole reduction of 90% is possible based on this result, with the lowest cost being of 21.2 B€ which is an increase of 44% of *TC* from A.ENV.8, however, as in the A.ENV case, the best environmental optimisation is obtained in B.ENV.10 for $E^{p,tot}$ equal to 0.175 Mt.

4.3 Multi-objective optimisation

With the multi-objective optimisation through the implementation of the ε-constrained method in the model the conflict between the two objective functions will be analysed. For the multi optimisation, the solution from the ECO cases with a carbon reduction of 50% are considered as economic optimum, while the environmental optimum is given from the relative ENV cases.

4.3.1 MULTI optimisation for Scenario A

From Scenario A it resulted that the same capture technology is always selected for both the ECO and ENV cases, and even for sequestration the model selects always an onshore one, with an exception in A.ENV.10 where there is one offshore sequestration. This means that the variability from the two cases is given mostly from the transport stage.

Table 4.8 – *step sl, net final CO_2 emissions E [Mt] and total cost TC [B€] for all the A.MULTI optimisations.*

Case		**ECO**										**ENV**
	sl	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
A.MULTI.5	*E [Mt]*	119	111	103	94.2	86.5	78.7	70.9	63.2	56.1	50.4	42.9
	TC[B€]	8.64	9.26	9.95	10.6	11.3	11.9	12.6	13.2	13.9	14.4	15.2
A.MULTI.8	*E [Mt]*	119	111	103	95.0	86.8	78.2	70.4	63.9	56.1	50.2	42.9
	TC[B€]	8.53	9.15	9.77	10.4	11.0	11.7	12.3	12.9	13.5	14.1	14.7
A.MULTI.10	*E [Mt]*	119	111	102	93.8	85.8	77.8	70.1	62.2	54.9	47.6	42.9
	TC[B€]	8.55	9.18	9.82	10.5	11.1	11.7	12.4	13.0	13.6	14.3	14.9

In Table 4.8 is reported a summary of the main results from each element calculated from the method to build the Pareto curve. *sl* is the surplus variable, it indicates how much the method moves and calculates a solution from one optimum to another one. When *sl* is equal to 0 there is the economic optimum from the ECO cases, while when *sl* is equal to 1 there is the solution from the ENV cases. In Figure 4.15, all the elements of A.MULTI.8 calculated from the method are plotted.

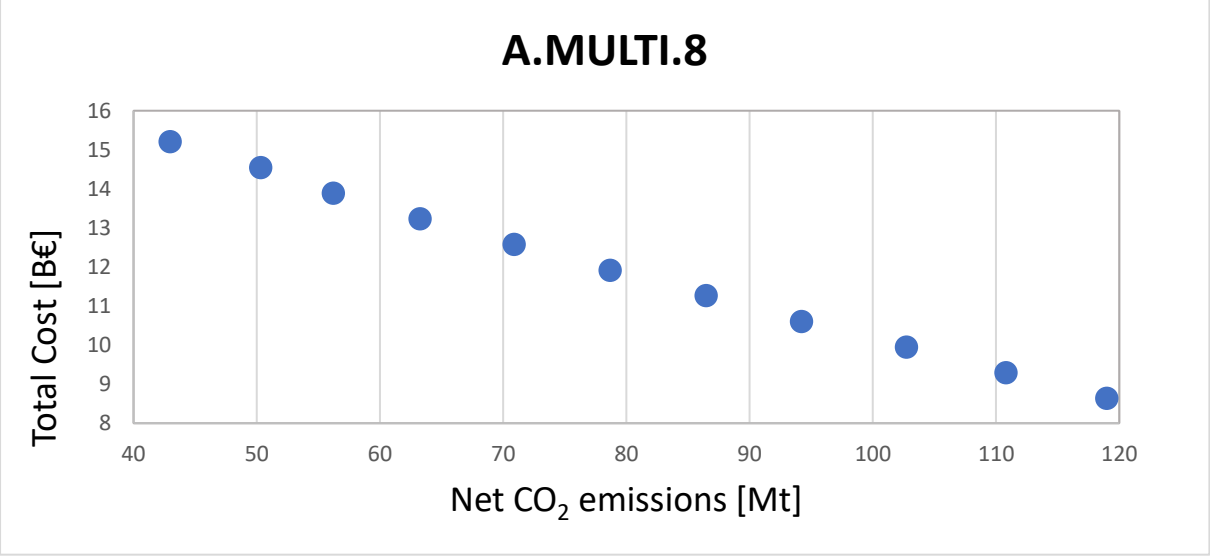


Figure 4.15 – *Plot of TC and E of all elements from A.MULTI.8 optimisation.*

From the figure the multi-objective optimisation of Scenario A shows a linear correlation between the economic and environmental objectives. This is caused by the fact that the only difference between the results of A.ECO.8 and A.ENV.8 is constituted by the volumes of CO2 captured, since the technology used is always the CaL. This just confirms the previous results for Scenario A in which this technology is the best one not only from an economic point of view but even from an environmental one, but because of this, there is not a real trade-off between the two objectives. The same conclusions can be applied even for the subcase with 5 and 10 clusters since the plot would be similar.

4.3.2 MULTI optimisation for Scenario B

In Table 4.9 the results (i.e.; *E* and *TC*) of every element calculated from the method are reported. In B.ENV there is an important change from all the other cases: the selection of the capture technology which is the MAL one instead of the CaL one. Because of this, the plot built with the elements of Table 4.9 in Figure 4.16 gives a Pareto curve, in which is possible to identify a trade-off, a compromise between the two best single-objective solutions.

Table 4.9 – *step sl, net final CO_2 emissions E [Mt] and total cost TC [B€] for all the B.MULTI optimisations.*

B.MULTI.5									
sl	0	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4
E [Mt]	119	111	102	93.7	85.4	76.8	68.8	60.9	53.0
TC[B€]	8.36	9.02	9.68	10.4	11.0	11.7	12.3	13.0	13.7
sl	0.45	0.5	0.52	0.6	0.7	0.75	0.8	0.9	1
E[Mt]	45.8	40.6	37.1	35.0	32.3	30.9	29.5	26.8	24.0
TC[B€]	14.3	15.0	15.2	16.3	17.7	18.3	19.0	20.3	21.7
B.MULTI.8									
sl	0	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4
E [Mt]	119	110	101	92.7	84.1	75.8	67.2	59.4	51.1
TC[B€]	8.29	8.93	9.57	10.2	10.9	11.5	12.2	12.8	13.5
sl	0.45	0.5	0.52	0.6	0.7	0.75	0.8	0.9	1
E[Mt]	45.0	37.4	36.7	34.6	32.0	30.6	29.3	26.6	24.0
TC[B€]	14.1	14.8	15.0	16.1	17.4	18.0	18.6	19.9	21.2
B.MULTI.10									
sl	0	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4
E [Mt]	119	110	101	92.3	83.5	75.0	67.2	58.3	50.0
TC[B€]	8.31	8.96	9.62	10.3	10.9	11.6	12.2	12.9	13.6
sl	0.45	0.5	0.52	0.6	0.7	0.75	0.8	0.9	1
E[Mt]	44.2	37.1	36.7	34.4	31.7	30.4	29.0	26.3	24.0
TC[B€]	14.2	14.9	15.1	16.2	17.5	18.1	18.8	20.1	21.4

For B.MULTI.5 and B.MULTI.10 there is no plot because it would be the same as for B.MULTI.8. In fact, the results of the same *sl* do not have a significant difference compared to the other cases and plotting the three Pareto curves on the same Figure, would just make them overlaps.

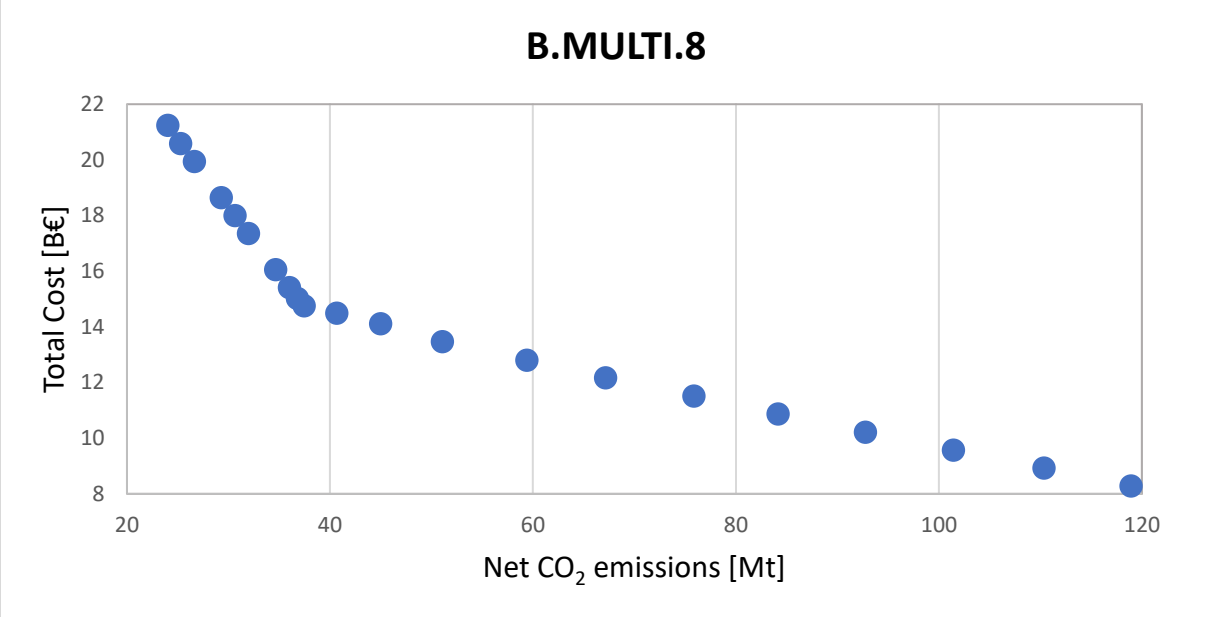


Figure 4.16 – *Plot of the solutions found from B.MULTI8 optimisation.*

From Figure 4.16 it is possible to identify where the best trade-off should be. It has a *TC* around 15 B€ and an *E* around 36-37 Mt. Within these ranges, when comparing to the numeric results in Table 4.9, the solution for *sl* equal to 0.52 fits them. Moreover, the solution from B.MULTI.8 has a lower *TC* and *E* compared to the other two subcases. In Table 4.10 more details from this solution are given.

Table 4.10 – *Costs and emissions of all B.MULTI.8 subcase for sl =0.5, in terms of: total costs TC [B€], capture cost TCC [B€], transport cost TTC [B€], sequestration cost TSC [B€] and their relative specific cost [€/t] expressed to the amount in tons [t] of overall sequestrated CO_2. The final net emission E [Mt], initial E^0 [Mt], additional ΔE [Mt], sequestrated E^{out} [Mt] and related to pumping $E^{p,tot}$ [Mt].*

Subcases	***TC***		***TCC***		***TTC***		***TSC***		***E***	E^0	**Δ*E***	E^{out}	$E^{p,tot}$
	[B€]	[€/t]	[B€]	[€/t]	[B€]	[€/t]	[B€]	[€/t]	[Mt]	[Mt]	[Mt]	[Mt]	[Mt]
B.MULTI.8	15.0	69.3	1.16	53.9	1.78	8.24	1.56	7.20	36.7	238	15.0	217	0.191

From Table 4.10 some important considerations can be done. First of all, the specific *TCC* is equal to 53.9 €/t, this means that the predominant technology is still the CaL but some other capture system is employed. To be more specific, the capture is done on all nodes, so it is like an ENV case, and in two nodes out of twenty-nine, the MAL technology is applied. This explains the

increase of 1.5 €/t from the CaL cost of 52.4 €/t. In this way a carbon reduction equal to 85% is achieved with a *TC* equal to 15.0 B€ with a specific cost of 69.3 €/t. As a matter of fact, *E* is equal to 36.7 Mt with 217 Mt of CO_2 sequestrated. Regarding the sequestration, the specific cost is always equal to *USC* (i.e., 7.20 €/t) meaning that there is only onshore sequestration. For the transport, *TTC* is nearly the same as in A.ENV.8 and B.ENV.8, although $E^{p,tot}$ is equal to 0.191 Mt which is higher than the other two subcases. Overall, this is like a slightly better optimised A.ENV.8 case regarding the emissions, introducing in some nodes the MAL technology.
For this case there is no SC representation of the infrastructure since it is the same as for A.ENV.8 (Figure 4.13) for which the same conclusions done about the sequestration nodes selected are still valid.

4.4 Computational performance

The time required for the solver to find a solution, the error (i.e.; relative gap) between the relaxed optimal solution with the best MILP solution and the number of single equations, single and discrete variables are used to evaluate the computational performance. The term single indicates the number of individual rows and column generated in the problem while the term discrete refers to a variable that can only assume specific values in an interval, like a binary variable that can only assume a value of 0 or 1. However, if the time and the relative gap are different for every subcase analysed, the numbers of single equations and variables are always the same for the number of clusters used and are reported in Table 4.11 with the non-zero elements, which are all the parameters or variables different from 0.

Table 4.11 – *Number of single equations, variables, discrete variables and non-zero elements based on clustering.*

Subcase	Single equations	Single variables	Discrete variables	Non-zero elements
5 Clusters	228712	127299	5729	649335
8 Clusters	281515	157479	9089	809867
10 Clusters	319317	179199	11329	924155

From Table 4.11, increasing the number of clusters increases the number of equations and variables, making the subcase more complex, because the solver has to deal with more calculations to do and doing more selections or decisions in the options.

In Table 4.12 the elapsed time and the relative gap for every subcase analysed are reported. The relative gap must be considered with the *optCR*, which is a value that can be set arbitrarily from the user and it is used for when the solver should stop its run. The solver will start its calculations and will continue to run until it does not find a solution which error is below the *optCR* value. For very complex models, time and computational resources used can become an issue, since the memory can be saturated losing all the progresses of the simulation, or it can take too much time like days if not weeks, before reaching the wanted optimality gap. Therefore *optCR* is set according to the problem. This model is not complex, and as a matter of fact an *optCR* of 0.01% is set for every subcase. A complex model would be the one presented by d'Amore and Bezzo (2017), in which its Scenario E has 1386644 variables, 77 times the number of the variables in the subcase with 10 clusters, and it took 21884 seconds to reach a solution with an optimality gap of 3.7 [%] (data taken from Table B1 in d'Amore and Bezzo (2017)).

For this model, all the calculations are done on a computer with a quad core CPU at 3.9 GHz and with 32 GB RAM.

Table 4.12 – *Elapsed time and relative gap of every subcase.*

Subcase	α	Elapsed time	Relative gap
	[%]	*[hh:mm:ss]*	*[%]*
A.ECO.5	50%	0:00:06	0.0094
A.ECO.8	50%	0:00:08	0.0004
A.ECO.10	50%	0:00:12	0.0016
A.ECO.5	30%	0:00:08	0.0
A.ECO.8	30%	0:00:05	0.0
A.ECO.10	30%	0:00:28	0.0059
A.ECO.5	70%	0:00:03	0.0034
A.ECO.8	70%	0:00:11	0.0064
A.ECO.10	70%	0:00:12	0.0008
A.ECO.5.OFF	50%	0:00:02	0.0011
A.ECO.8.OFF	50%	0:00:03	0.0023
A.ECO.10.OFF	50%	0:00:08	0.0076
B.ECO.5	50%	0:00:05	0.0
B.ECO.8	50%	0:00:11	0.0045
B.ECO.10	50%	0:00:23	0.0008
A.ENV.5		0:00:18	0.0
A.ENV.8		0:00:12	0.0
AENV.10		0:00:17	0.0
B.ENV.5		0:00:04	0.0028
B.ENV.8		0:00:15	0.0
B.ENV.10		0:00:18	0.0012
A.MULTI.5		0:06:12	<0.01
A.MULTI.8		0:21:29	<0.01
A.MULTI.10		0:15:01	<0.01
B.MULTI.5		0:06:22	<0.01
B.MULTI.8		0:20:57	<0.01
B.MULTI.10		0:21:55	<0.01

From Table 4.12 it is interesting that the highest elapsed time for a single-objective optimisation is of 28 seconds for A.ECO.10 with a carbon reduction target of 30%, following behind it the B.ECO.10 with 23 seconds. The lowest elapsed time instead for a single objective optimisation is

for A.ECO.5.OFF with 2 seconds. However, all the single-objective subcases do not need even 30 seconds to achieve a solution below *optCR,* confirming that the model is quite fast. About the relative gap, only A.ECO.5 – 50% has the highest error equal to 0.0094%, while all the other subcases have a lower error or so low that it is considered equal to 0. When the relative gap is equal to 0, system gives as message: proven optimal solution and not solution satisfies tolerances, meaning that the relaxed optimal solution coincides with the optimal MILP one. For the multi-objective optimisation, the time is from a minimum of 6 minutes and 22 seconds from B.MULTI.5 to a maximum of 21 minutes and 55 seconds for B.MULTI.10. In the MULTI cases, it can happen often that some solutions are infeasible because of the constraints and for how the ε-constrained method calculates the elements of the Pareto curve, however, for all the iterations done in every case, there was no infeasible solution and all relative gaps are below *optCR* always equal to 0.01%. Overall, changing the carbon reduction target in the ECO cases or some parameters like in Scenario B, or forcing to choose only one option like an offshore sequestration, does not increase the computational burden of the model and thus the time needed for the solver to calculate an optimal solution.

Conclusion

This Master's Thesis aimed at designing an optimal carbon capture and sequestration supply chain for the Italian cement industry through a mixed integer linear programming modelling framework. The objective functions were the minimisation of the total cost required for the installation and operation of the supply chain and the minimisation of the net carbon dioxide emissions (comprehensive of indirect emissions due to the operation of capture plants). In particular, the model was optimised for three main scenarios: an economic case to minimise total costs, an environmental optimisation to minimise the net CO_2 emission, and a bi-objective optimisation minimising both costs and emissions to analyse the conflict between these possible conflicting objectives.

Calcium looping emerged as the best technology in the optimisation of both costs and emissions under consideration of an Italian energy mix in the calculation of indirect emissions due to capture. In fact, this technology was always selected for installation on cement plants, due to its high efficiency (i.e., 91%) and relatively low cost (52.4 €/t). In the multi-objective case studies, calcium looping emerged always again as the best capture technology and thus, no trade-offs emerged between economic and environmental and optimisations. The environmental optimisation showed that the maximum net carbon reduction target that could be achieved from Italian cement industry is equal to 81% of original emissions without capture. Sequestration was always operated onshore to minimise costs apart from few case studies, in which the optimal supply chain design contemplated offshore storage in the Ionian Sea (Calabria Ionica), due to the vicinity of a carbon collection cluster. Regarding the costs, capture and sequestration costs do not show any variability among subcases, and only the optimisation of the transport stage entails marginal differences. Because of this, the case with 8 clusters always resulted as the one with the lowest transport costs. In a test imposing to only sequester offshore the higher transport costs was determined in the case with 10 clusters. In general, the capture costs share contributes to 82% of the total cost, while the sequestration cost amounts to 11%, and the transport cost to 7%. In the end, for the scenario considering the carbon intensity of the Italian energy mix, the specific cost of the supply chain varies from 64.5 €/t for a reduction of 50% to 67.8 €/t for the environmental optimisation.

The main consequence of using renewable energy is the decrease of the additional emissions related to the capture operation. In the economic optimisation, the calcium looping is confirmed again as the best technology, however the total cost is decreased because it needs to capture less CO_2 to achieve a reduction of 50%. But, in the environmental optimisation the technology selected was the membrane-assisted liquefaction with an efficiency of 90% and a cost of 83.5 €/t. This is caused by the fact that the technology uses only electrical power to operate, meaning that its additional emissions are null using renewable energy. This allowed to reach a carbon reduction of 90% equal to its efficiency, with a specific cost of 99.1 €/t. In the multi-optimisation the difference in the technology selected between the two optimisations, managed to find an optimal trade-off configuration between the two optimums, in which the main technology used is always the calcium looping, but the membrane-assisted liquefaction is introduced in some nodes. The result was a supply chain configuration with a specific cost of 69.3 €/t and a carbon reduction of 85%.

An important aspect to consider is related to the fact that many of the sequestration basins modelled in this study are onshore, likely near cities, and the population acceptance should be taken into consideration to understand the social response towards the implementation of such infrastructures.

A possible improvement or development of this model could consist in implementing further industrial emissions sources like refineries so as to expand the modelling framework towards a larger introduction of carbon capture and storage technologies within the Italian context

Bibliography

AITEC, *Rapporto di sostenibilità AITEC 2017*. (Available at: https://www.aitecweb.com/Portals/1/Repository/Pubblico/Area%20Tecnica/Pubblicazioni/Rapporto_di_sostenibilit%C3%A0_AITEC_2017.pdf?ver=2018-12-10-171307-560)

BP (2018). BP Statistical review of World Energy 2018. London, UK.

CEMCAP, (2018) (Available at: https://www.sintef.no/projectweb/cemcap/)

CEPCI, (2018). Chemical engineering plant cost index [WWW Document]. (Available at: https://www.chemengonline.com/pci-home)

d'Amore, F., & Bezzo, F. (2017). *Economic optimisation of European supply chains for CO 2 capture, transport and sequestration.* International Journal of Greenhouse Gas Control, 65, 99–116. doi:10.1016/j.ijggc.2017.08.015

Donda, F., Volpi, V., Persoglia, S., & Parushev, D. (2011). *CO2 storage potential of deep saline aquifers: The case of Italy.* International Journal of Greenhouse Gas Control*,* 5(2), 327–335. doi:10.1016/j.ijggc.2010.08.009

EEA, European Environment Agency ,(2018), CO_2 Emission Intensity, (available at: https://www.eea.europa.eu/data-and-maps/daviz/co2-emission-intensity-5#tab-googlechartid_chart_11)

E-PRTR, European Pollution Release and Transfer Register. (Available at: https://prtr.eea.europa.eu/#/home)

EU GeoCapacity Project, 2009. Assessing European Capacity for Geological Storage of Carbon Dioxide: GeoCapacity Final Report. (Available at: www.geology.cz/geocapacity/publications)

Hills, T., Leeson, D., Florin, N., & Fennell, P. (2015). Carbon Capture in the Cement Industry: Technologies, Progress, and Retrofitting. Environmental Science & Technology, 50(1), 368–377. doi:10.1021/acs.est.5b03508

IEA (2015). Energy and Climate Change - World Energy Outlook Special Report, IEA, Paris, France.

IEA (2016). World Energy Outlook, International Energy Agency of the Organisation for Economic Co-operation and Development (OECD/IEA). IEA, Paris, France.

IPCC, 2005. In: Metz, B., Davidson, O., de Conick, H.C., Loos, M., Meyer, L.A. (Eds.), IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change. Cambridge University Press Cambridge, United Kingdom and New York, NY, USA (442 pp.)

IPCC, 2013: Summary for Policymakers. In: *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

IPCC, 2014. In: Fischedick M., J. Roy, A. Abdel-Aziz, A. Acquaye, J. M. Allwood, J.-P. Ceron, Y. Geng, H. Kheshgi, A. Lanza, D. Perczyk, L. Price, E. Santalla, C. Sheinbaum, and K. Tanaka, 2014: Industry. In: Climate Change 2014: Mitigation of Climate Change. Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Edenhofer, O., R. Pichs-Madruga, Y. Sokona, E. Farahani, S. Kadner, K. Seyboth, A. Adler, I. Baum, S. Brunner, P. Eickemeier, B. Kriemann, J. Savolainen, S. Schlömer, C. von Stechow, T. Zwickel and J.C. Minx (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

IPCC (2018). *IPCC Special Report, Global Warming of 1.5°C*. INTERGOVERNMENTAL PANEL ON CLIMATE. Prepared by Working Group III of the Intergovernmental Panel on Climate Change. Cambridge University Press, New York, U.S.A.

ISPRA, (2018), Fattori di emissione atmosferica di gas a effetto serra e altri gas nel settore elettrico. (Available at: http://www.isprambiente.gov.it/files2018/pubblicazioni/rapporti/R_280_18_Emissioni_Settore_Elettrico.pdf)

J. B. MacQueen (1967): "*Some Methods for classification and Analysis of Multivariate Observations*", Proceedings of 5-th Berkeley Symposium on Mathematical Statistics and Probability, Berkeley, University of California Press, 1:281-297

MacDowell, N., Florin, N., Buchard, A., Hallett, J., Galindo, A., Jackson, G., Fennell, P. (2010). An overview of CO2 capture technologies. Energy & Environmental Science, 3(11), 1645. doi:10.1039/c004106h

Laumanns, M., Thiele, L., & Zitzler, E. (2006). *An efficient, adaptive parameter variation scheme for metaheuristics based on the epsilon-constraint method.* European Journal of Operational Research, 169(3), 932–942. doi:10.1016/j.ejor.2004.08.029

UNFCCC (2015). Paris Agreement. FCCC/CP/2015/L.9/Rev1. (Available at: http://unfccc.int/resource/docs/2015/cop21/eng/l09r01.pdf.)

Voldsund, M., Gardarsdottir, S., De Lena, E., Pérez-Calvo, J.-F., Jamali, A., Berstad, D., Chao Fu, Romano M., Roussanaly S., Anantharaman R., Hoppe H., Sutter D., Mazzoti M. Gazzani M, Cinti G., Jordal, K. (2019). Comparison of Technologies for CO2 Capture from Cement Production—Part 1: Technical Evaluation. Energies, 12(3), 559. doi:10.3390/en12030559

Zhang, Z. X., Wang, G. X., Massarotto, P., & Rudolph, V. (2006). *Optimization of pipeline transport for CO2 sequestration*. Energy Conversion and Management, 47(6), 702–715. doi:10.1016/j.enconman.2005.06.001

ZEP, *The Costs of CO_2 Capture, Transport and Storage*, (Available at: https://www.globalccsinstitute.com/archive/hub/publications/119811/costs-co2-transport-post-demonstration-ccs-eu.pdf)