

This document provides supplementary information on the results obtained under realistic model–data mismatches and on the relationship between MER and TUR.

Table S1. Realistic model–data mismatches for each station estimated following the methodology in Sect. 3.5 of the main paper. The asterisk (*) marks ICOS stations with available observations used in the mismatch calculation.

Station I.D.	Model-data mismatch (ppb)	Station I.D.	Model-data mismatch (ppb)
BRM*	38	IT-PCm	38
CGR	21	IT-Ren	25
CHI	46	IT-SR2	65
CMN*	32	IT-Sas	19
CUR	19	IT-Tor	32
ECO	23	IT-TrF	33
ERS*	28	JFJ*	15
HEI*	55	KAS*	25
HPB	29	KIT*	27
HUN*	29	KRE*	23
IPR*	75	LHW*	38
IT-BCi	29	LMP*	26
IT-BFt	75	LMT	19
IT-Col	22	MDN	17
IT-Cp2	48	MRG	19
IT-Lpd	16	OHP*	22
IT-Lsn	40	OPE*	24
IT-MBo	31	POT	24
IT-Niv	27	PRS*	14
IT-Noe	18	SSL*	20
IT-Niv	27	VND	35
IT-Noe	18	ZSF	19
IT-Oxm	53		

Table S2. MER values obtained with non-uniform model-data mismatch for all network scenarios, regions, emission categories and seasons.

		SCENARIO	1	2	3	4	5	6	7	8	9	10	11	12
REGION	SECTOR	SEASON												
ALL OF ITALY	TOTAL	FULL YEAR	11	17	18	19	18	17	17	17	17	17	23	30
		DJF	11	14	17	17	15	15	15	14	14	16	21	30
		MAM	14	18	19	17	18	18	19	18	18	18	22	30
		JJA	10	19	21	21	20	19	20	20	20	20	26	31
		SON	9	13	15	17	15	14	14	15	14	14	20	29
	NATURAL	FULL YEAR	14	20	21	22	21	21	21	20	20	20	26	32
		DJF	15	17	19	18	18	18	17	17	17	18	22	29
		MAM	16	19	21	18	20	20	20	20	19	19	24	31
		JJA	12	24	24	26	25	25	26	25	25	25	31	35
		SON	12	15	16	20	16	16	16	16	15	15	22	28
	ANTHROPOGENIC	FULL YEAR	4	6	6	7	7	6	6	6	6	6	8	14
		DJF	4	5	6	7	6	6	6	6	5	6	9	16
		MAM	5	7	8	8	7	8	8	7	7	8	8	14
		JJA	3	5	6	6	6	5	6	6	5	6	7	11
		SON	3	6	6	7	7	6	7	7	6	6	9	16
NORTHERN ITALY	TOTAL	FULL YEAR	16	22	24	23	22	22	22	22	22	23	26	34
		DJF	16	19	23	19	20	18	19	19	19	21	24	36
		MAM	20	26	29	27	27	27	27	27	27	27	30	37
		JJA	14	22	24	23	23	22	22	23	22	24	26	32
		SON	10	15	15	16	15	15	15	15	15	15	17	28
	NATURAL	FULL YEAR	21	26	28	27	27	26	26	26	26	27	29	36
		DJF	21	22	27	23	24	22	22	22	22	25	28	37
		MAM	24	29	33	30	29	29	29	29	29	29	34	41
		JJA	16	27	26	28	27	27	27	27	26	29	29	34
		SON	17	19	17	20	20	19	18	19	19	19	18	25
	ANTHROPOGENIC	FULL YEAR	5	9	9	9	9	9	9	9	9	9	10	17
		DJF	5	8	9	9	8	8	8	8	8	8	10	18
		MAM	7	11	11	11	11	11	11	11	11	11	12	18
		JJA	4	8	8	8	8	8	8	8	8	9	8	13
		SON	4	8	7	9	8	8	8	8	8	8	9	18
CENTRAL ITALY	TOTAL	FULL YEAR	11	15	17	17	16	15	15	15	15	15	20	30
		DJF	12	13	14	17	15	13	13	13	13	15	19	29
		MAM	9	9	9	6	11	9	9	9	9	9	8	24
		JJA	11	18	20	23	20	18	18	18	18	18	26	33
		SON	10	17	21	20	18	17	17	17	16	18	23	30
	NATURAL	FULL YEAR	15	19	21	21	21	19	19	19	19	20	24	33
		DJF	15	16	16	16	19	16	17	16	16	18	19	29
		MAM	12	12	11	9	14	12	11	12	12	12	10	23
		JJA	13	22	25	28	24	22	23	22	22	22	32	37
		SON	13	20	26	23	21	20	20	21	19	21	28	34
	ANTHROPOGENIC	FULL YEAR	2	3	4	4	3	3	3	3	3	3	5	12
		DJF	3	3	4	6	4	4	3	3	3	4	7	15
		MAM	3	4	4	4	4	4	4	4	4	4	5	10
		JJA	1	2	2	2	2	2	2	2	2	2	3	10
		SON	3	3	4	3	4	3	4	4	4	4	5	12
SOUTHERN ITALY	TOTAL	FULL YEAR	3	9	9	13	11	11	12	12	10	9	20	25
		DJF	2	6	6	11	7	7	7	7	6	5	15	20
		MAM	3	5	5	6	6	8	9	8	7	5	13	20
		JJA	1	14	15	15	17	15	18	18	17	14	26	28
		SON	5	9	9	16	11	10	11	11	9	9	22	28
	NATURAL	FULL YEAR	3	10	11	14	12	14	13	12	11	10	22	25
		DJF	2	7	7	10	8	10	7	7	7	7	13	15
		MAM	4	6	6	6	6	9	12	9	7	6	16	21
		JJA	1	18	19	20	20	21	22	21	21	18	31	33
		SON	6	5	5	16	7	8	7	7	5	5	21	26
	ANTHROPOGENIC	FULL YEAR	2	3	3	4	4	3	4	4	3	3	7	12
		DJF	2	3	3	5	4	3	4	3	3	3	7	13
		MAM	1	2	3	3	2	3	3	3	3	2	3	9
		JJA	1	3	3	4	4	2	3	4	3	3	6	9
		SON	2	4	4	5	6	4	5	6	4	4	10	15

Table S3. TUR values obtained with non-uniform model-data mismatch for all network scenarios, regions, emission categories and seasons.

		SCENARIO	1	2	3	4	5	6	7	8	9	10	11	12
REGION	SECTOR	SEASON												
ALL OF ITALY	TOTAL	FULL YEAR	26	37	41	41	38	38	38	37	37	38	47	55
		DJF	20	29	38	32	29	30	29	29	29	29	42	50
		MAM	23	40	42	44	41	41	41	41	40	41	48	54
		JJA	29	38	43	42	39	39	39	38	39	39	49	56
		SON	30	39	41	43	41	41	41	40	40	40	47	56
	NATURAL	FULL YEAR	30	43	48	47	43	44	44	43	43	43	54	61
		DJF	27	35	45	39	36	36	36	35	35	35	49	57
		MAM	27	44	47	49	45	45	46	45	45	45	55	60
		JJA	34	44	49	48	45	45	46	45	45	45	55	62
		SON	33	46	49	50	48	48	48	47	47	47	55	63
	ANTHROPOGENIC	FULL YEAR	8	15	18	15	15	15	15	14	15	16	20	31
		DJF	9	19	23	18	19	19	19	19	19	20	25	38
		MAM	3	10	13	10	10	10	10	10	10	12	16	23
		JJA	6	12	15	13	13	13	13	12	12	14	19	27
		SON	12	17	19	17	18	17	17	17	17	17	20	32
NORTHERN ITALY	TOTAL	FULL YEAR	28	36	42	36	36	36	36	36	36	37	43	51
		DJF	23	31	42	31	30	31	31	30	31	31	43	51
		MAM	27	39	43	40	39	39	39	39	39	41	44	49
		JJA	29	35	42	36	36	36	36	35	36	37	43	50
		SON	31	37	39	37	37	37	37	37	37	38	40	51
	NATURAL	FULL YEAR	35	42	49	43	42	42	42	42	42	43	50	57
		DJF	32	35	48	36	35	35	35	35	35	36	49	56
		MAM	33	47	51	48	47	47	47	47	47	48	52	53
		JJA	39	44	50	44	44	44	44	44	44	45	50	55
		SON	39	43	46	43	43	43	43	43	43	44	47	56
	ANTHROPOGENIC	FULL YEAR	12	21	27	22	22	22	22	21	21	24	29	40
		DJF	14	27	34	28	27	28	28	27	27	30	35	49
		MAM	7	16	21	16	16	16	16	16	16	18	23	30
		JJA	11	18	24	19	19	18	19	18	18	21	27	37
		SON	15	23	27	23	24	24	24	23	23	25	27	40
CENTRAL ITALY	TOTAL	FULL YEAR	22	27	30	32	27	27	27	27	27	27	35	48
		DJF	16	19	23	23	19	19	19	19	19	19	28	41
		MAM	19	29	31	37	30	30	29	30	29	29	39	50
		JJA	25	29	32	33	29	29	29	29	29	29	36	47
		SON	25	28	30	31	29	29	28	28	29	29	34	48
	NATURAL	FULL YEAR	27	32	36	39	33	33	32	33	33	33	43	54
		DJF	23	26	32	32	27	26	26	26	26	26	37	51
		MAM	23	32	36	43	34	32	32	33	32	32	46	54
		JJA	29	33	37	37	34	34	33	34	34	34	40	52
		SON	30	35	39	39	37	36	36	36	36	36	44	55
	ANTHROPOGENIC	FULL YEAR	4	5	5	5	5	5	5	5	5	5	7	24
		DJF	5	5	6	5	6	6	6	6	5	6	7	21
		MAM	4	6	6	7	6	6	6	6	6	6	8	25
		JJA	2	3	3	4	3	3	3	3	3	3	4	20
		SON	4	7	7	7	7	7	7	7	7	7	8	29
SOUTHERN ITALY	TOTAL	FULL YEAR	4	28	29	34	31	32	32	31	30	29	43	46
		DJF	2	26	27	32	29	29	29	27	27	26	39	42
		MAM	3	25	25	29	27	28	30	29	28	25	40	43
		JJA	6	32	32	38	34	35	35	34	34	32	45	47
		SON	5	29	29	33	31	33	33	32	30	29	44	49
	NATURAL	FULL YEAR	5	34	35	41	36	38	39	37	36	34	51	54
		DJF	3	34	35	42	35	37	37	35	34	34	48	51
		MAM	4	24	24	28	26	28	31	28	27	24	45	47
		JJA	6	38	38	45	39	41	42	39	39	38	53	56
		SON	7	37	38	40	39	42	43	41	39	37	55	58
	ANTHROPOGENIC	FULL YEAR	2	4	4	4	7	4	5	5	4	4	10	15
		DJF	2	5	5	4	10	6	5	5	5	5	11	16
		MAM	1	4	4	4	5	4	6	5	4	4	10	17
		JJA	2	4	5	5	7	5	6	5	5	4	10	10
		SON	2	3	3	3	7	3	4	4	3	3	8	17

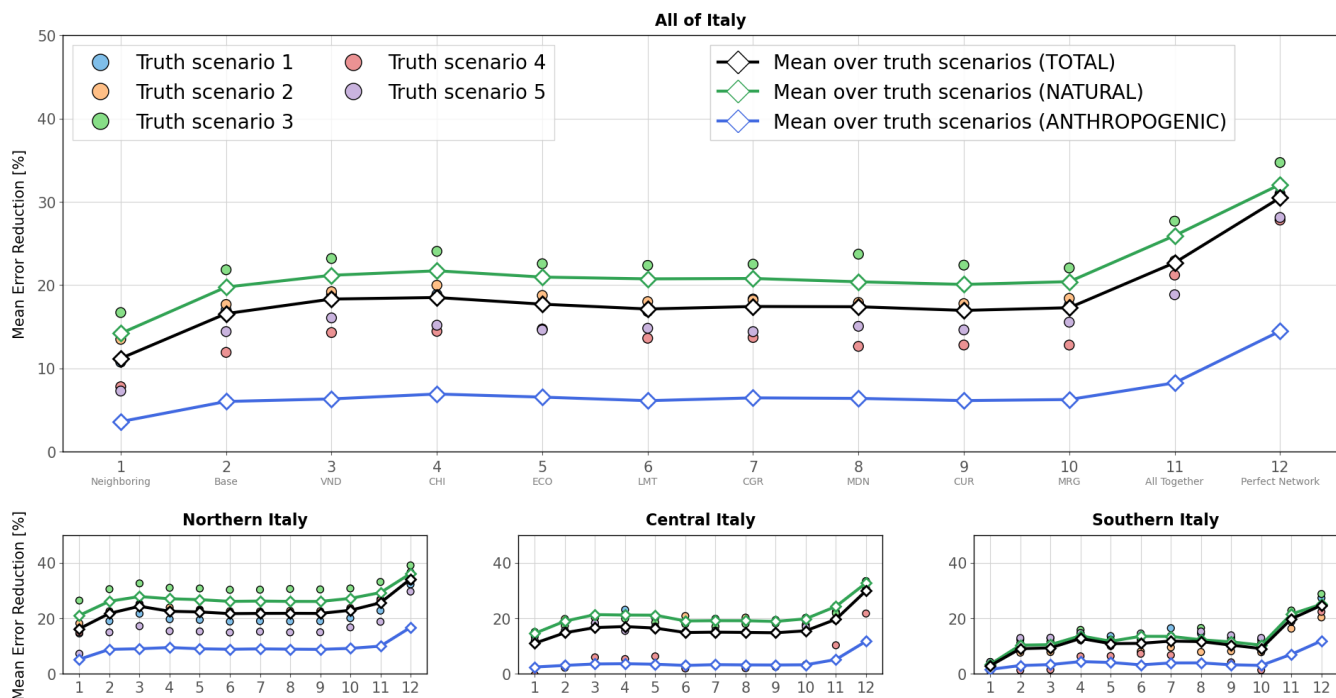


Figure S1. MER obtained with non-uniform model-data mismatch. MER is displayed for each scenario over all of Italy, Northern Italy, Central Italy, and Southern Italy. Black lines represent MER for total emissions (mean over truth scenarios). Green and blue lines represent MER for natural and anthropogenic emissions, respectively. Coloured circles show MER for total emissions under different truth scenarios.

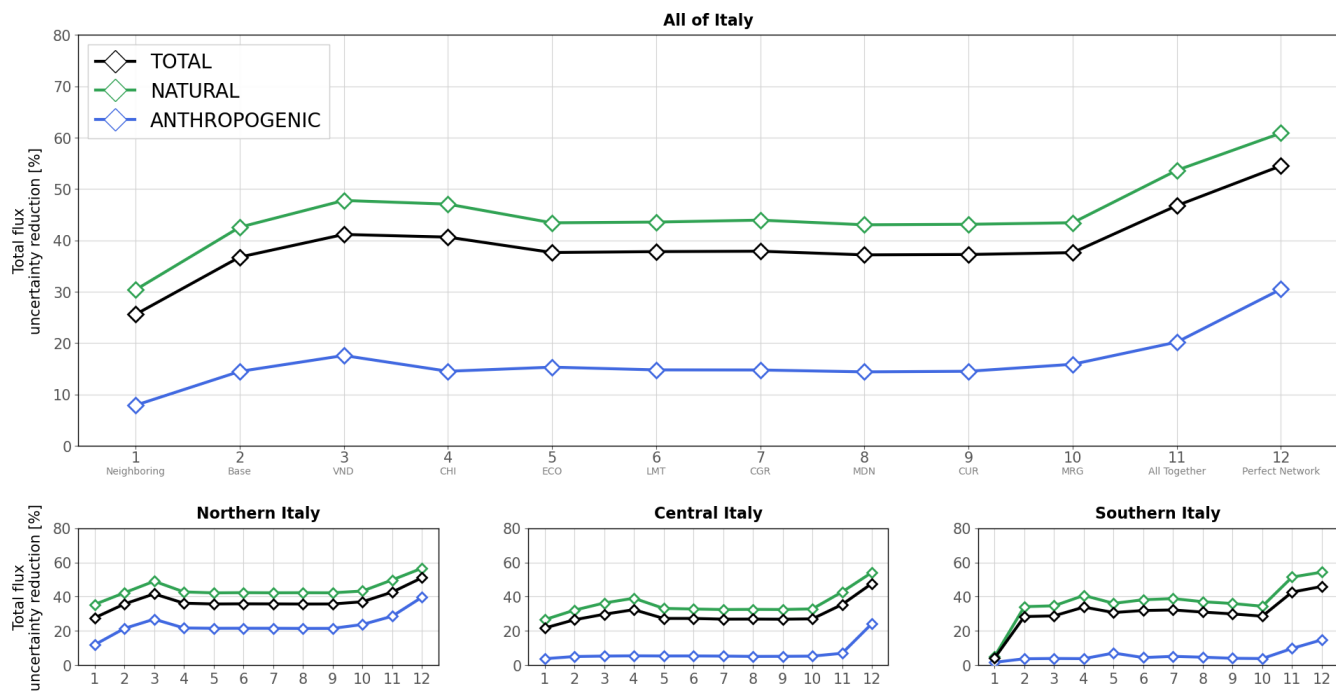


Figure S2. TUR obtained with non-uniform model-data mismatch. TUR is displayed for each scenario over all of Italy, Northern Italy, Central Italy, and Southern Italy. Black lines represent TUR for total emissions (mean over truth scenarios). Green and blue lines represent TUR for natural and anthropogenic emissions, respectively. Coloured circles show TUR for total emissions under different truth scenarios.

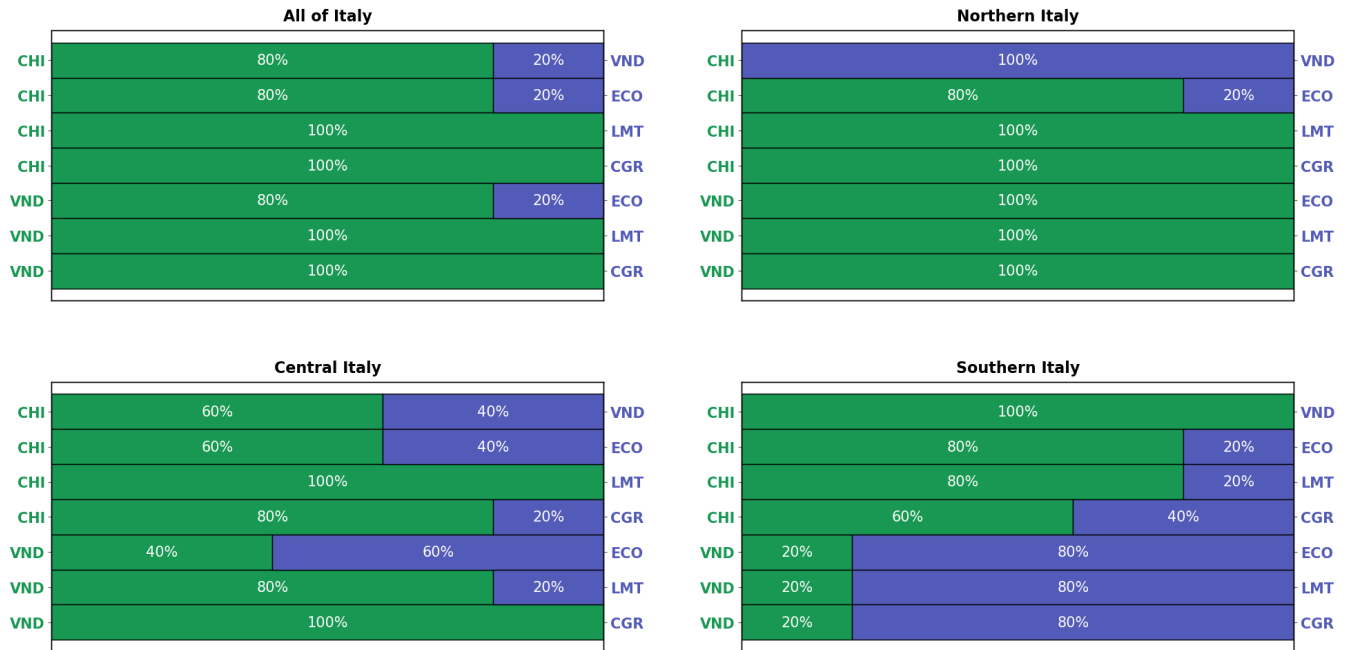


Figure S3. Pairwise comparison between network scenarios with a non-uniform model-data mismatch. In each comparison, the horizontal bar is divided into two sub-bars (green and blue). The green sub-bar (and its associated percentage) represents the fraction of truth scenarios in which adding the first station (green) yields a greater improvement in MER than adding the second station (blue). Conversely, the blue sub-bar (and its percentage) indicates the fraction of truth scenarios where adding the second station (blue) leads to a larger MER improvement than the first. For example, CHI outperforms VND in terms of MER for all of Italy in 80 % of the truth scenarios.

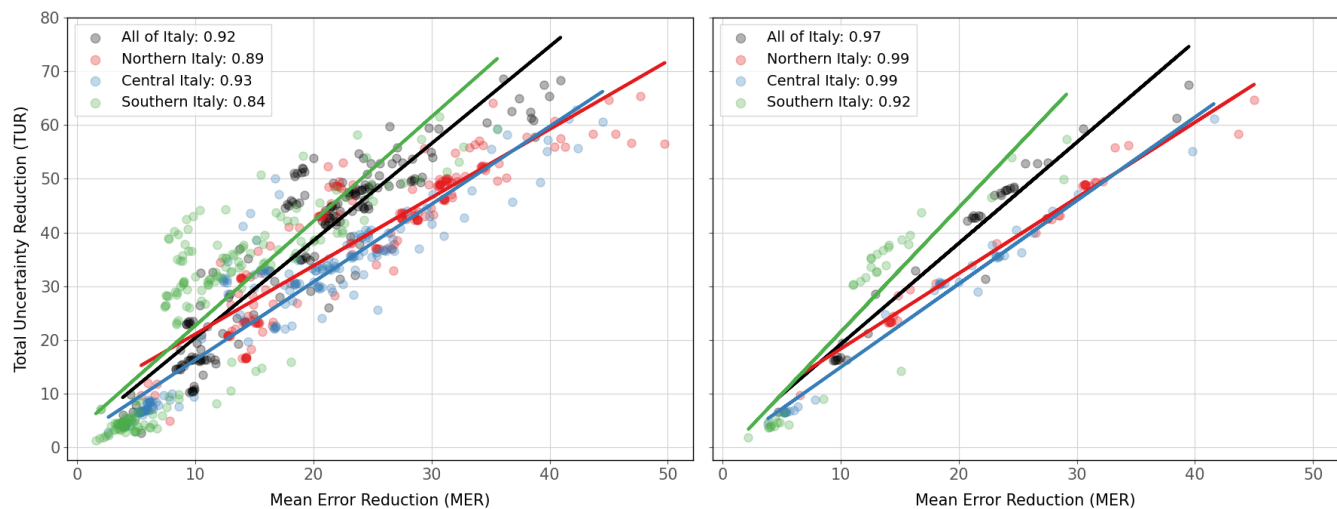


Figure S4. Relationship between MER and TUR, differentiated by region. Each dataset includes a fitted regression line, with the corresponding Pearson correlation coefficient indicated in the legend. The left panel shows the regression based on all data, including seasonal variations, while the right panel excludes seasonality, displaying only full-year values.