

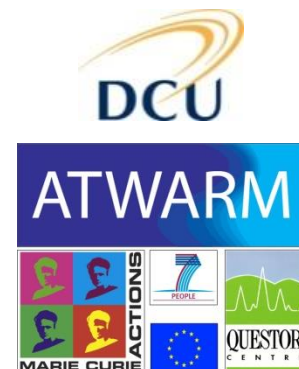
# Approaches and Analytical Tools to Disentangle Point and Diffuse Sources of Nitrate Contamination

**Cecilia Fenech**

**Supervisors:** A. Morrissey, K. Nolan, L. Rock

Water: The Greatest Global Challenge

Thursday 16<sup>th</sup> May, 2013



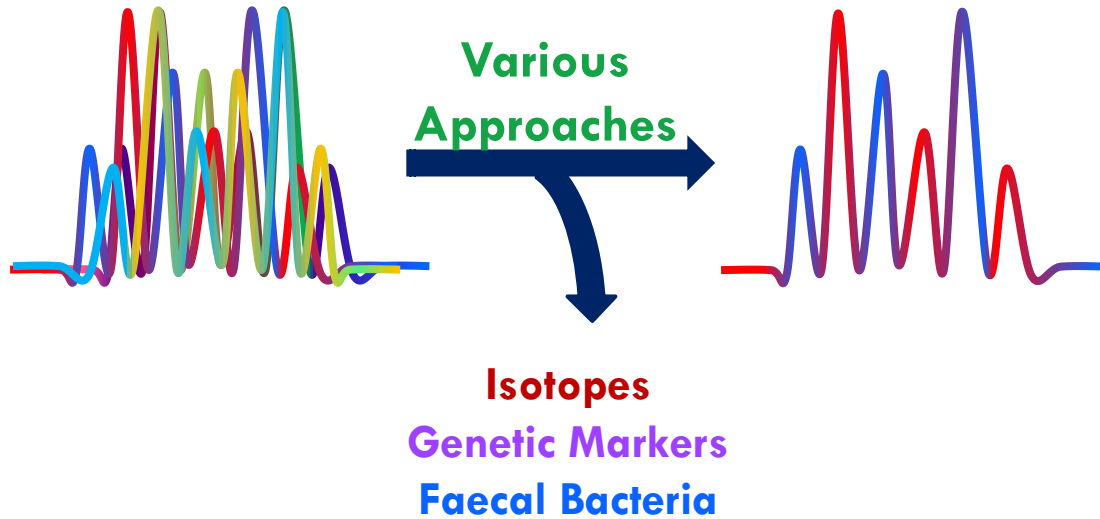
# Research Question



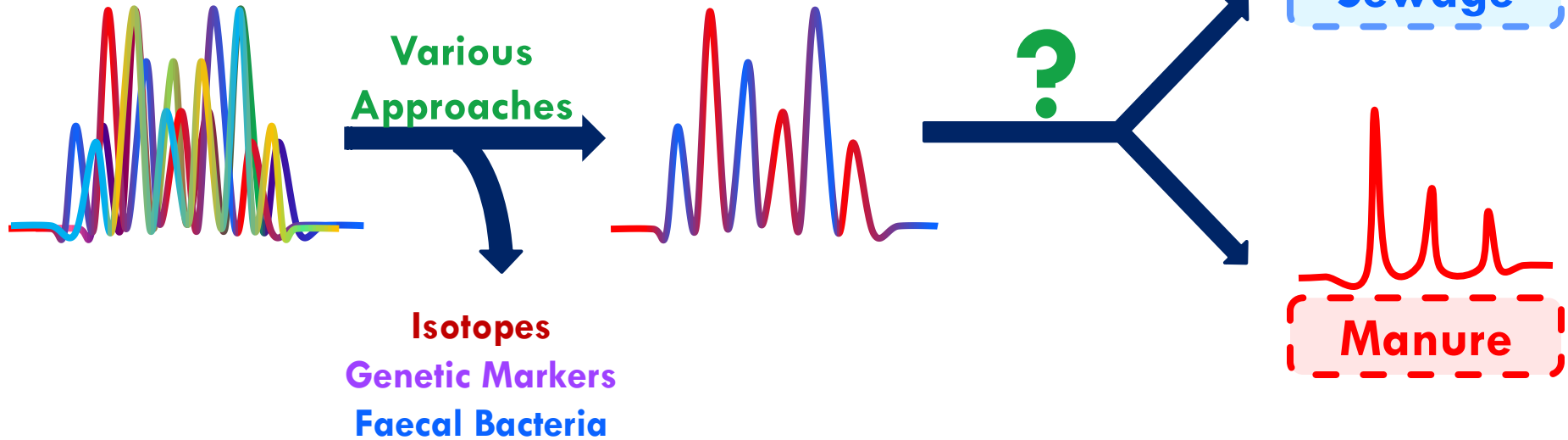
**How can we determine the source of nitrate contamination in rivers and lakes?**



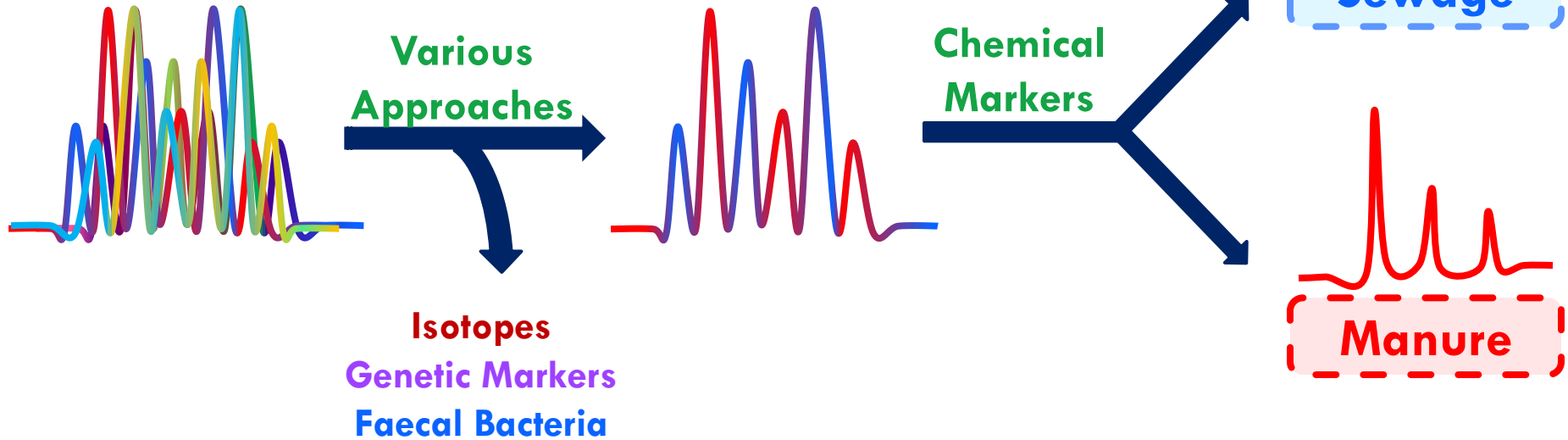
# Differentiating Nitrate Sources



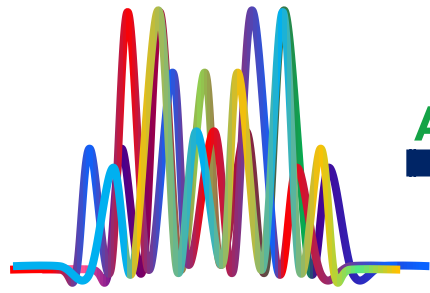
# Differentiating Nitrate Sources



# Differentiating Nitrate Sources

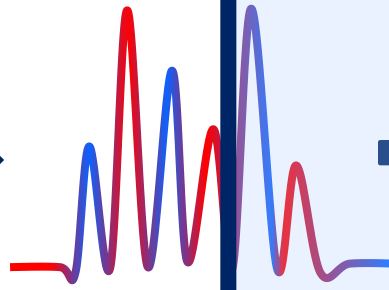


# Differentiating Nitrate Sources

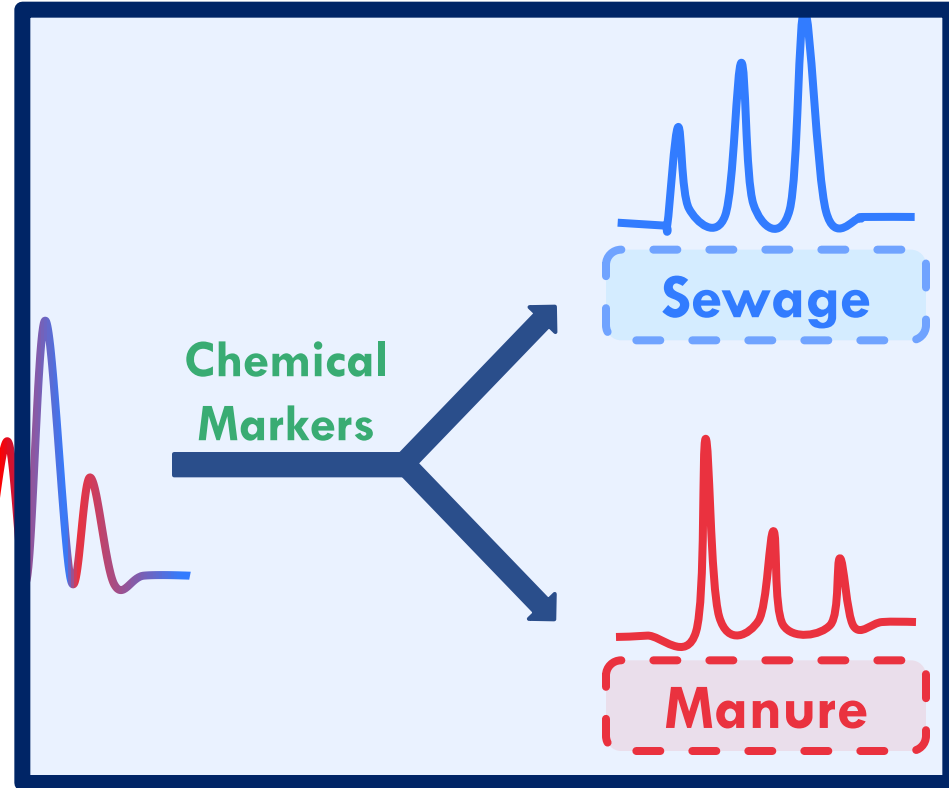


Various  
Approaches

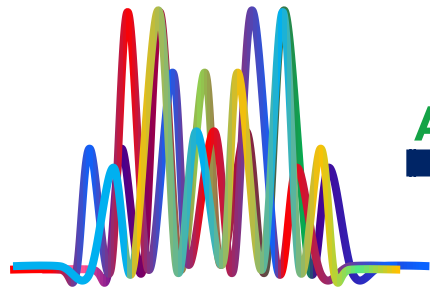
Isotopes  
Genetic Markers  
Faecal Bacteria



Chemical  
Markers

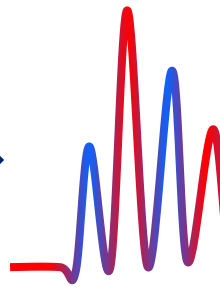


# Differentiating Nitrate Sources



Various  
Approaches

Isotopes  
Genetic Markers  
Faecal Bacteria



Chemical  
Markers  
**Chemical  
Markers**

Manure



# Differentiating Nitrate Sources



Various  
Approaches

Decision Tool

Isotopes  
Genetic Markers  
Faecal Bacteria

Chemical  
Markers

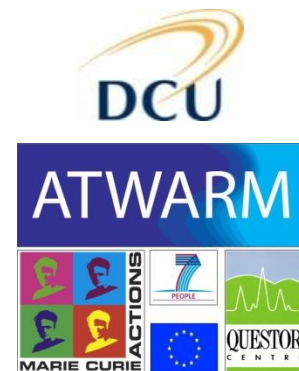


Introduction

# Chemical Markers

Decision Tool

Conclusions



Chemical Markers

Research Questions

**Which Markers?**

# Which Markers?

How do we detect them?

Where do they come from?

# Which Markers?

How do we detect them?

Where do they come from?

'Traditional'

Alternatives

# Which Markers?

How do we detect them?

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Alternatives

# Analytical Suite

**Sewage**



**Acetaminophen**  
**Cotinine**  
**Caffeine**  
**Carbamazepine**  
**Diltiazem**  
**Diphenhydramine**

**Manure**



**Tylosin**  
**Enrofloxacin**  
**Lincomycin**  
**Sulfadimethoxine**

# Which Markers?

How do we detect them?

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'Traditional'

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# Which Markers?

How do we detect them?

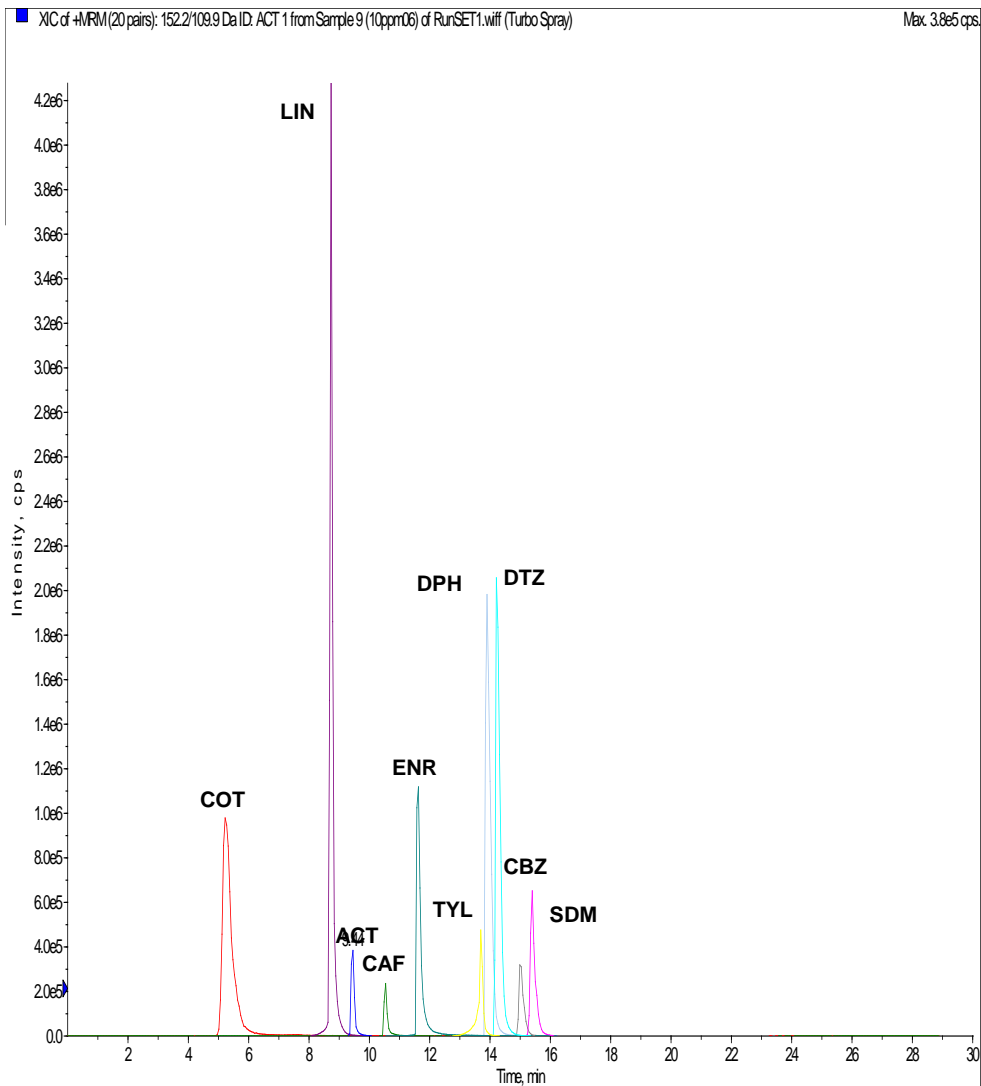
Where do they come from?

'Traditional'

Alternatives



# Chromatography

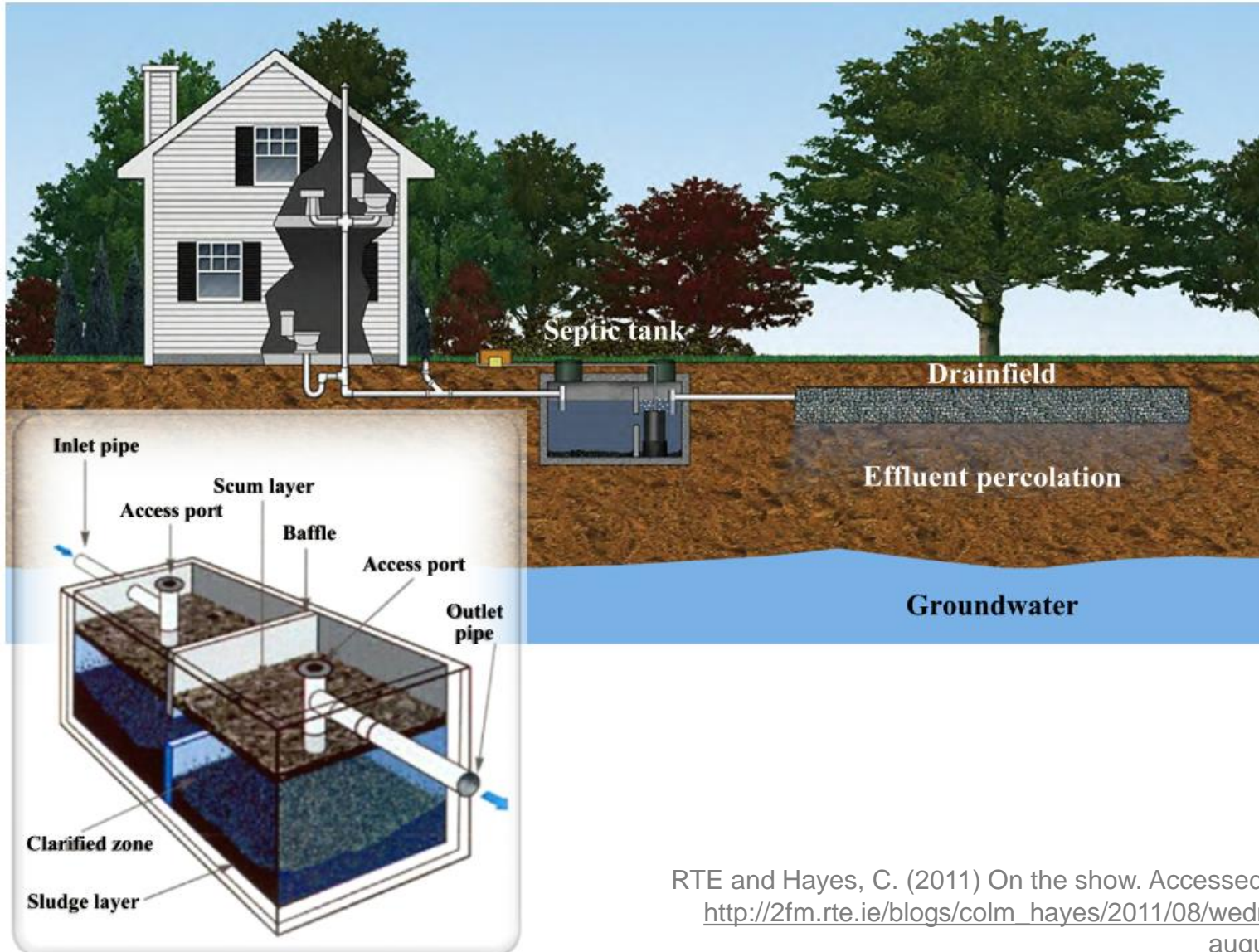


Cartridge	<b>Waters Oasis HLB</b>
Column	<b>Phenomenex Luna PFP</b>
MS Method	<b>MRM</b>
Instruments	<b>1. AB Sciex Triple Quad 2. Bruker Ion Trap</b>
Linearity	<b>5 ng/L - 500 µg/L</b>
LOQ	<b>5ng/L – 50ng/L</b>
LOD	<b>50pg/L - 5ng/L</b>

# Sampling Programme



# Septic Systems



RTE and Hayes, C. (2011) On the show. Accessed 03/10 2012.  
[http://2fm.rte.ie/blogs/colm\\_hayes/2011/08/wednesday-10th-august-2011.html](http://2fm.rte.ie/blogs/colm_hayes/2011/08/wednesday-10th-august-2011.html)

# Which Markers?

How do we detect them?

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# Which Markers?

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# Alternatives



# Alternatives



LC-MS

NMR

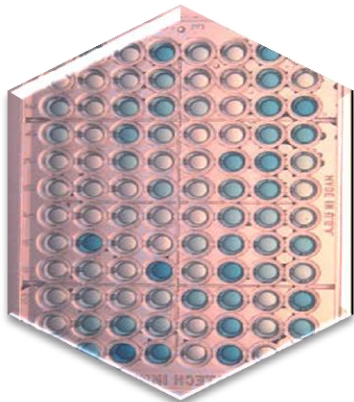


# Alternatives



LC-MS

NMR



Immuno  
-assays



# Immunoassays

- LOD: 12 ng L<sup>-1</sup>
- Minimal Sample Preparation
- High Throughput
- Potential for Multiplex Screening

# Which Markers?

How do we detect them?

Where do they come from?

'Traditional'

Alternatives

# Which Markers?

How do we detect them?

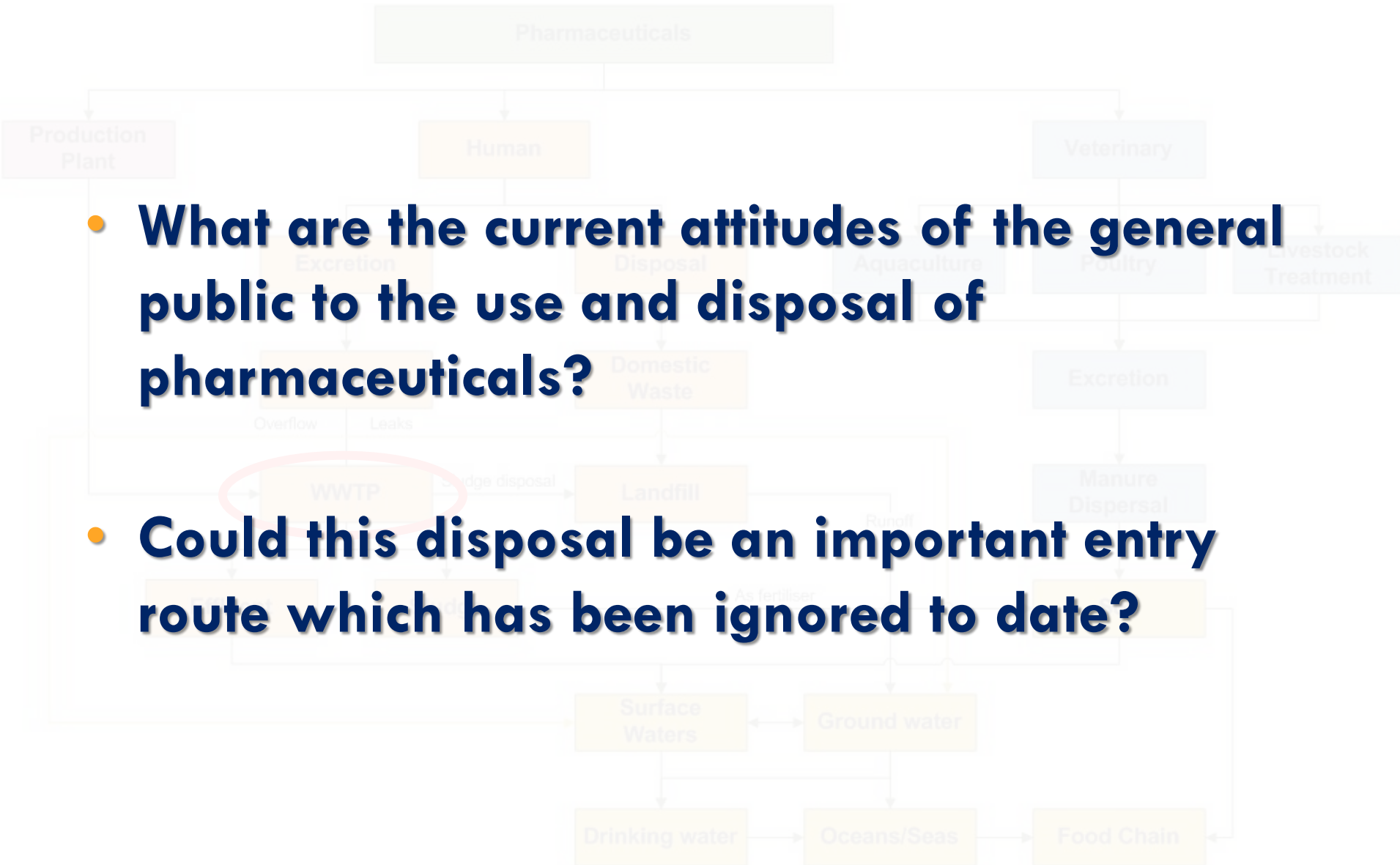
Where do  
they come  
from?

'Traditional'

Alternatives

# Pharmaceutical Sources

- **What are the current attitudes of the general public to the use and disposal of pharmaceuticals?**
- **Could this disposal be an important entry route which has been ignored to date?**



# Sample Characteristics



1,449 respondents



## Demographics

- 98% European
- Widespread age, education and residence



## Outcome

- Disposal in sewer system is minimal
- Lack of education on correct disposal

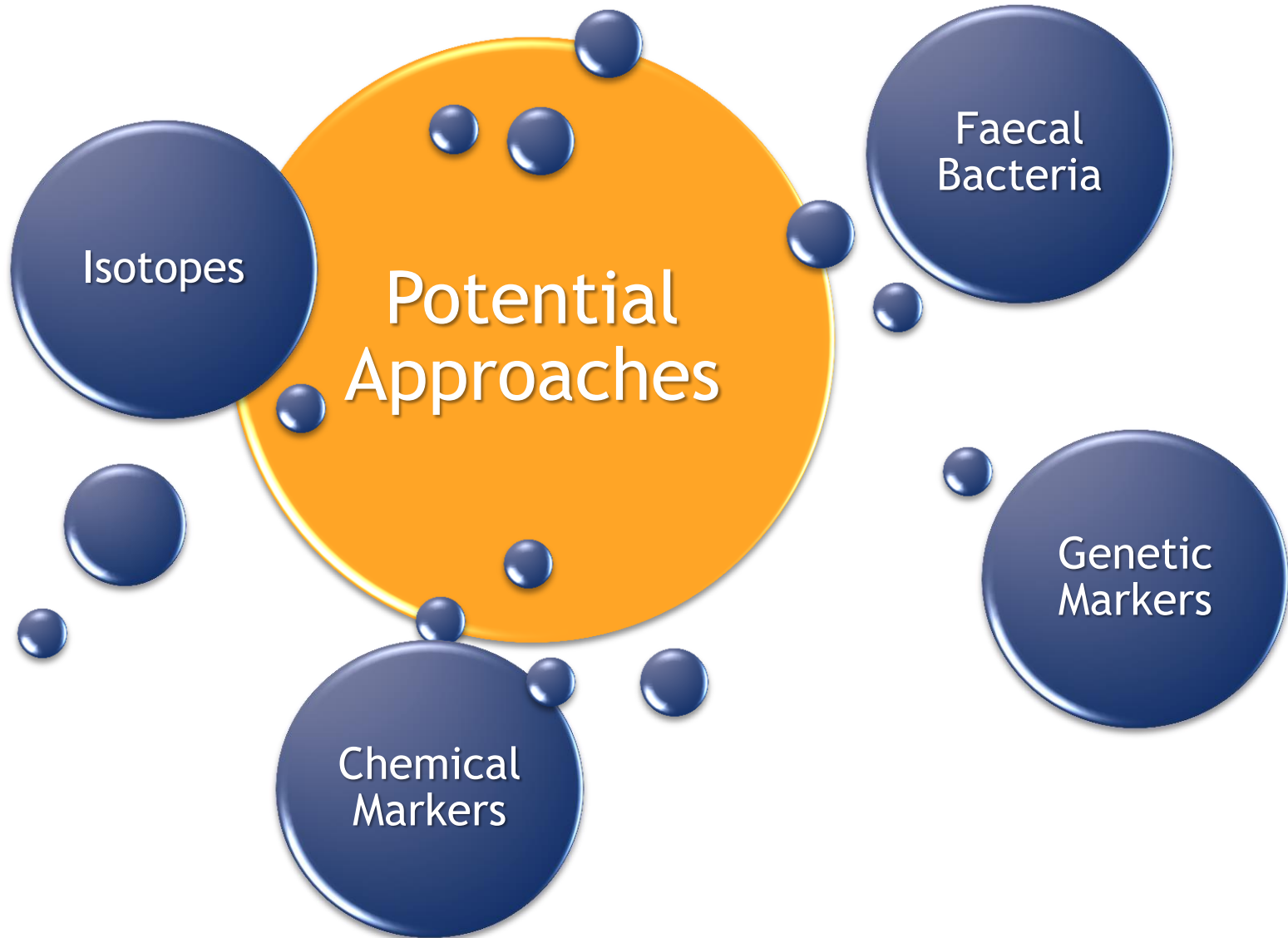
Introduction  
Chemical Markers

# Decision Tool

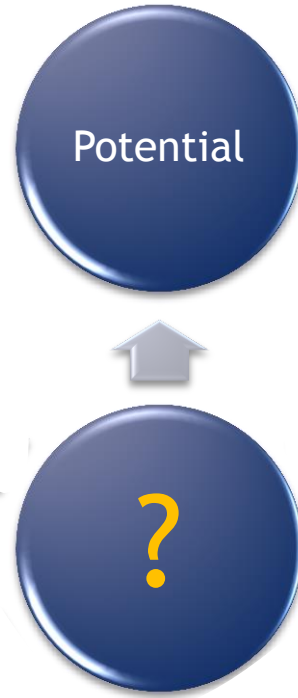
Conclusions



# NSD

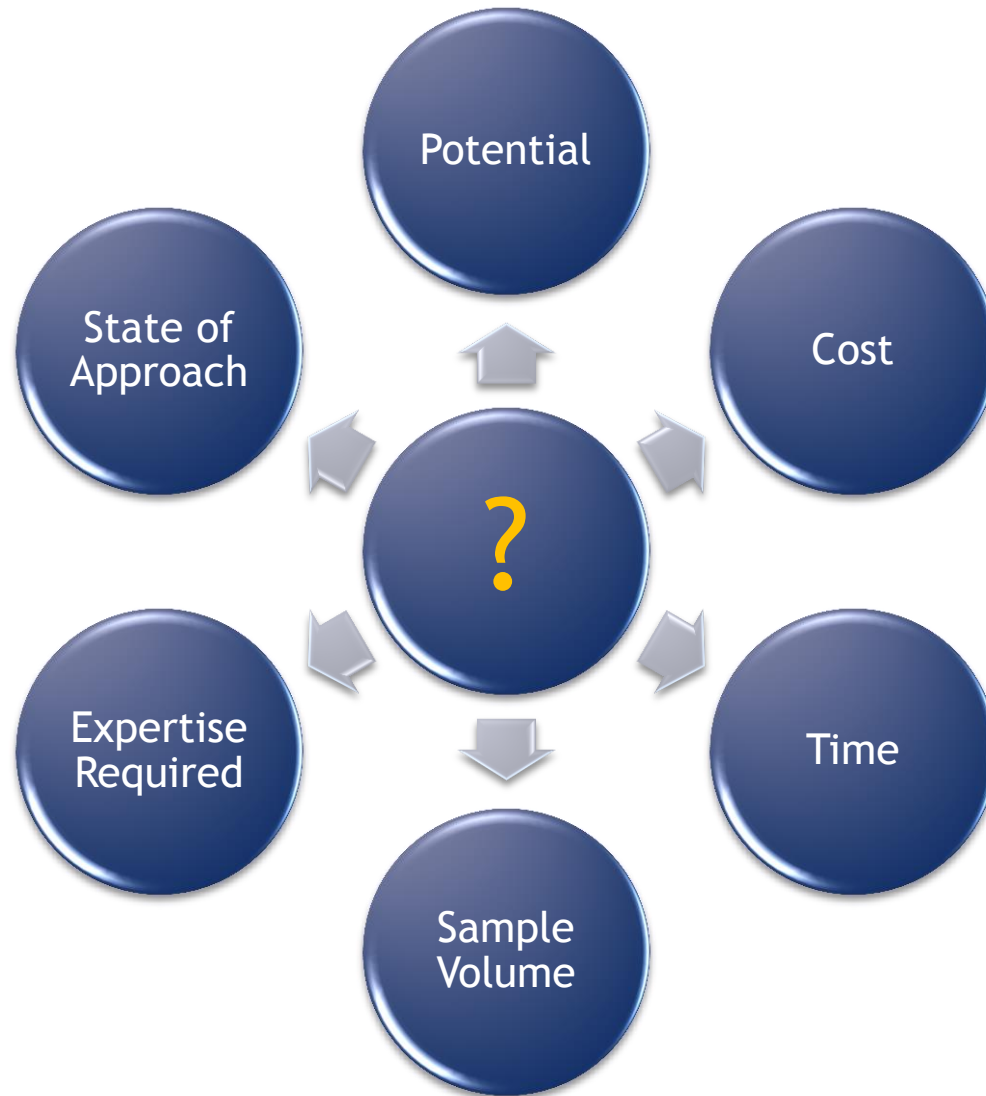


# Considerations

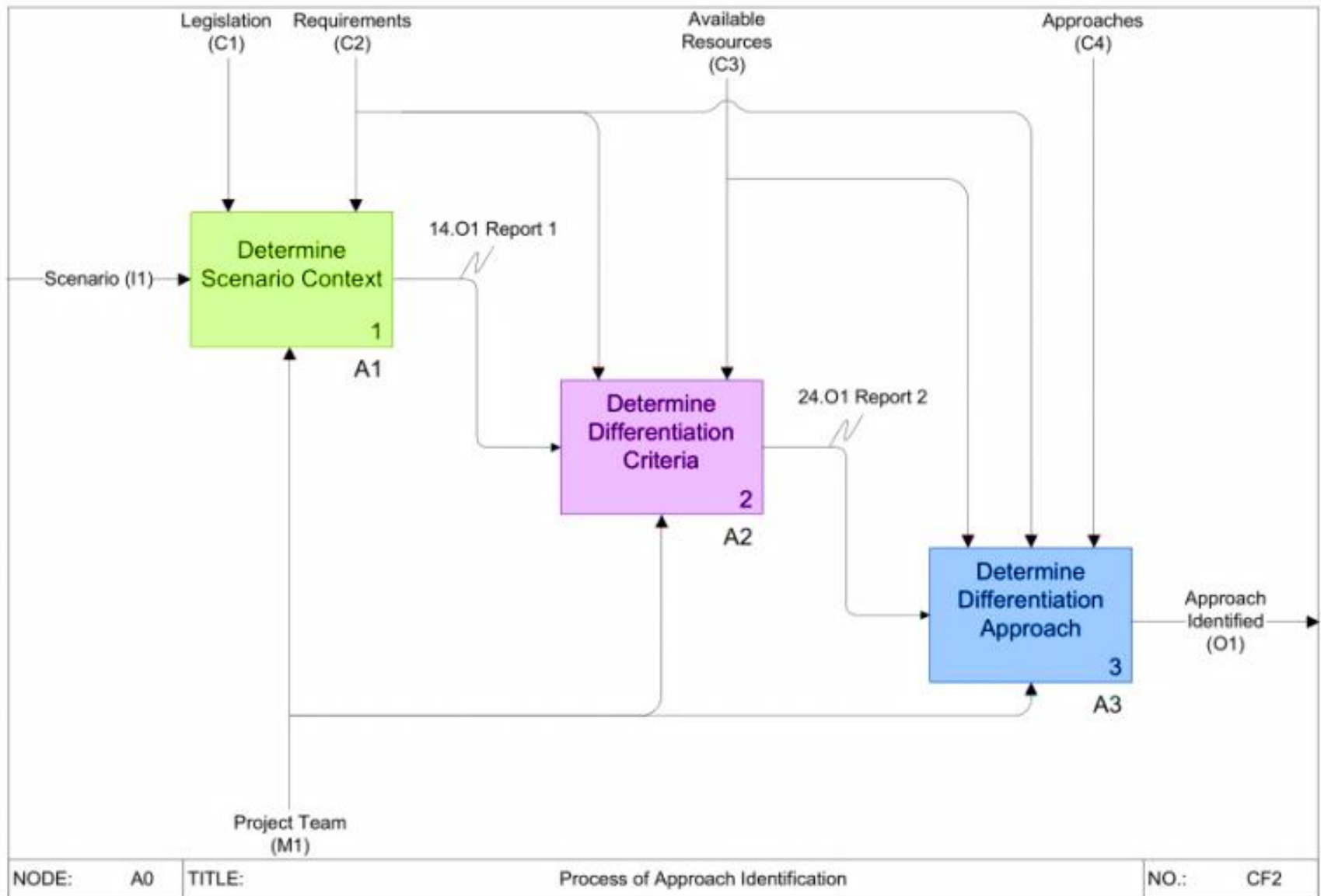




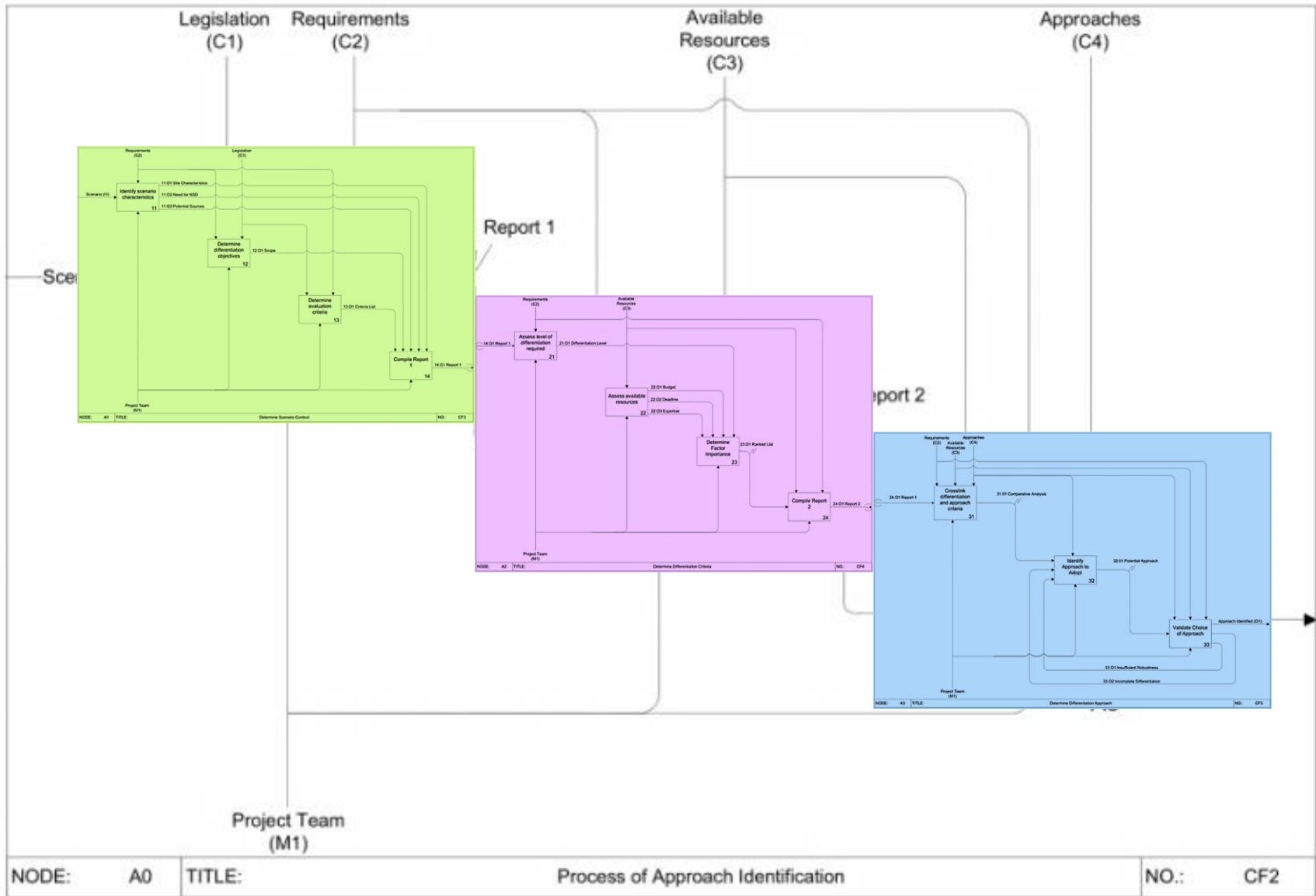
# Considerations



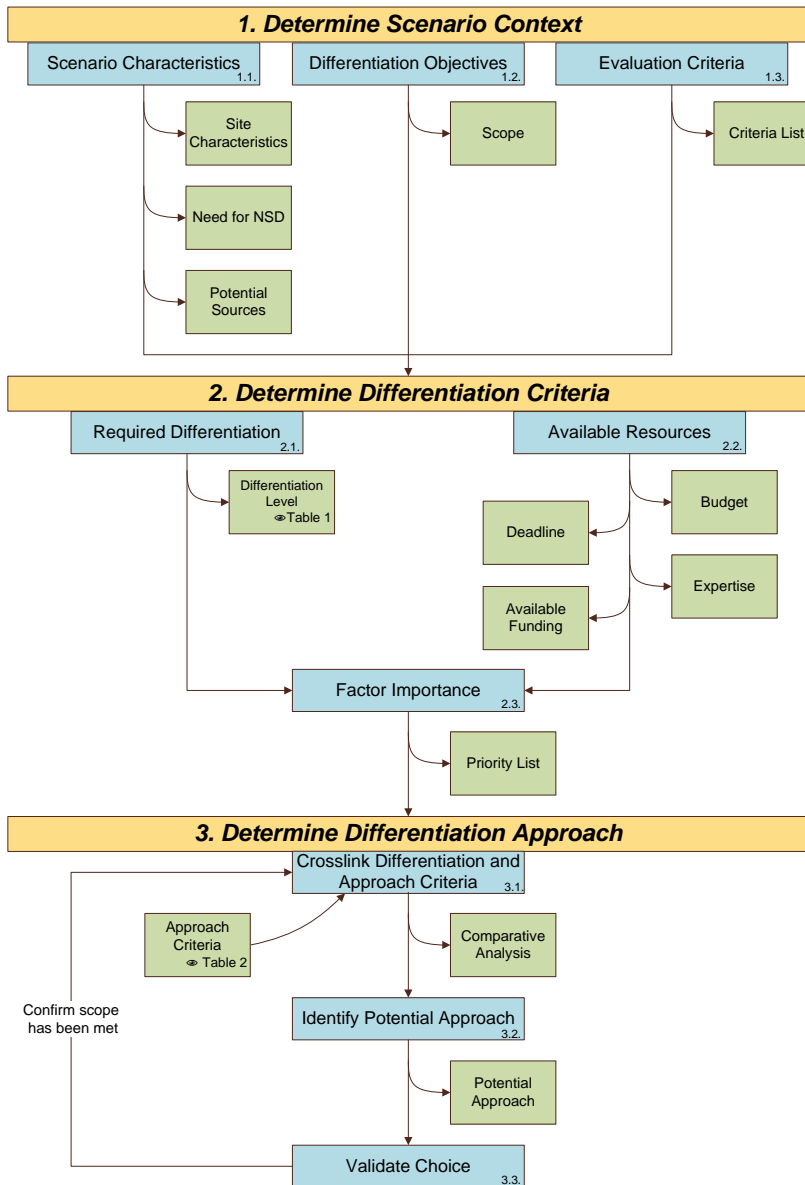
# IDEF0 Model



# IDEF0 Model



# Decision Tool

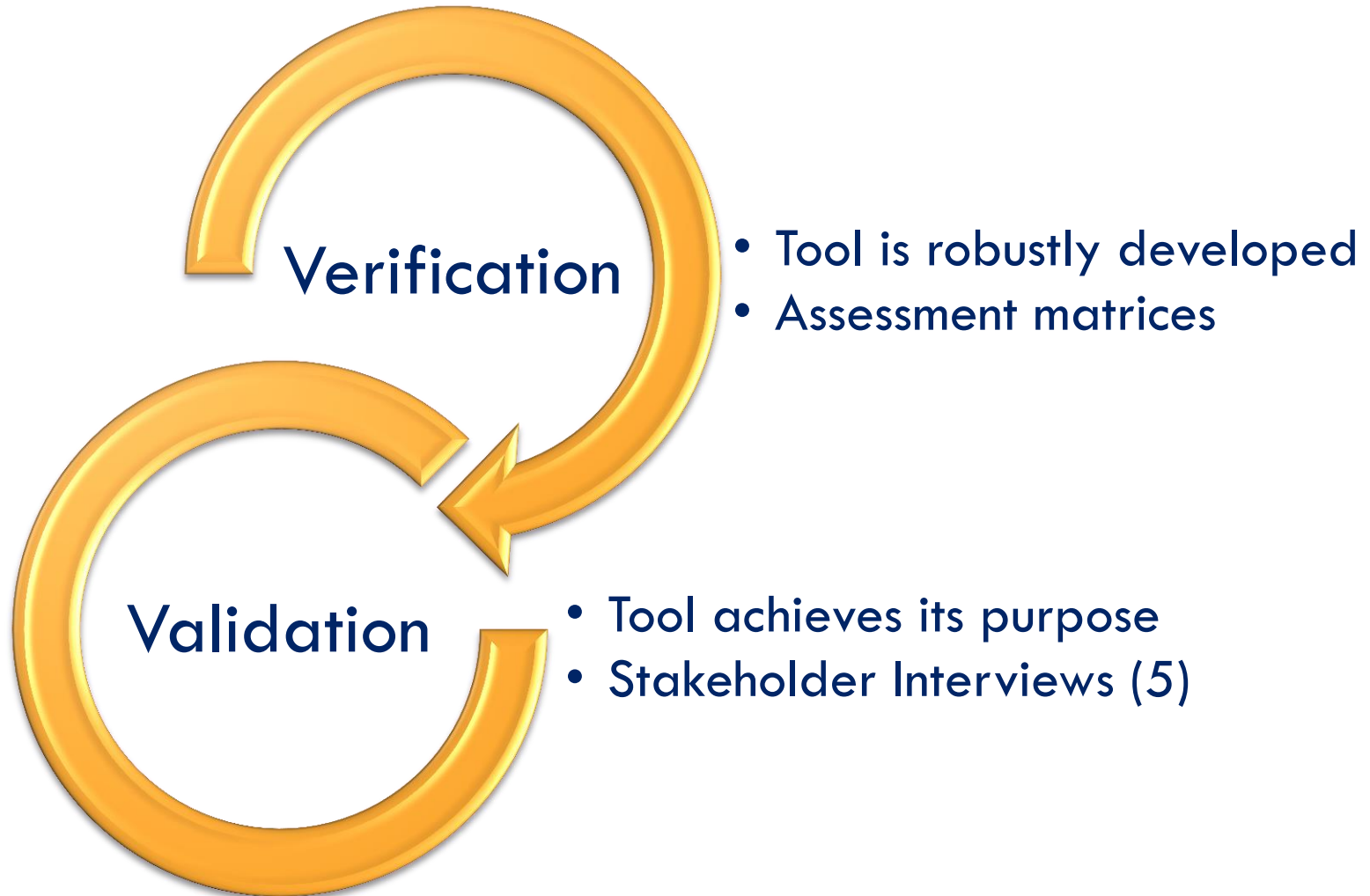


Sources of Contamination	Approaches			
	Nitrate Isotopes	Genetic Markers	Micro-biological	Chemical Markers
Manure (organism 1)	1	1	1	1
Manure (organism 2)		2		
Manure (organism x)		3		
Raw sewage	2	4	3	2
Treated sewage		3		
Nitrate in precipitation	2	NA	NA	NA
Nitrate in fertiliser	3			
Soil nitrogen	4			
Desert nitrate deposits	5			
Ammonium in Fertiliser	6			

	Nitrate Isotopes	Genetic Markers	Micro-biological	Chemical Markers
Instrumentation	IRMS	Various	Incubator	Various
Time Requirement	Days	Hours	Days	Hours
Sample Volume	Millilitres	Millilitres	Centilitres	Litres
Multi-Source Determination	No	Yes	No	Yes
Typical Cost	++	+++	+	++
Level of Expertise	+++	+++	+	+++
State of Approach	+++	+	+++	++
Technique Availability	+	++	+++	++

# Reporting Tool

# Tool Evaluation



Introduction  
Chemical Markers  
Decision Tool

# Conclusions



# Research Focus



**Differentiating the source of nitrate contamination in rivers and lakes**



# Publications

- The potential for a suite of isotope and chemical markers to differentiate sources of nitrate contamination: A review. *Water research*, 46(7):2023-2041, 2012.
- Disposal of non-ingested pharmaceuticals within households: Is it a waste management concern? *CIWM Magazine*, December 2012.
- Attitudes towards the use and disposal of unused medications in two European countries. *Waste Management*, 33(2): 259-261, 2013.
- Advances in water quality monitoring of inorganics: current trends. *JWARP*, 5(4A): 40-48, 2013.
- Differentiation of nitrates sources: An environmental forensics approach. *Science Career Article*. RESB, In Press.
- A multi-residue method for the analysis of human and veterinary chemical markers within surface waters: An environmental forensics approach. *Environmental Pollution*, Submitted.



# Acknowledgements





**Thank you!**