THE DEVELOPMENT OF A COMPACT TIME-DOMAIN NUCLEAR MAGNETIC RESONANCE SYSTEM FOR IN SITU MEASUREMENT

Master's Defense

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WHAT IS NUCLEAR MAGNETIC RESONANCE (NMR)?

- "a powerful analytical technique that uses the magnetic properties of atomic nuclei to study molecular structure, dynamics, and interactions." – Google AI Overview
- Choose a reference isotope
  - H^1, C^{13}, P^{31} are the most common
- Measure that isotope and other magnetic material
  - By probing magnetization

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HOW CAN IT BE USED?

- Biology
  - Protein structure and interactions
- Chemistry
  - Material Composition
- Medicine
  - MRI
- Physics
  - Nanoscale NMR

PHYSICS BEHIND NMR

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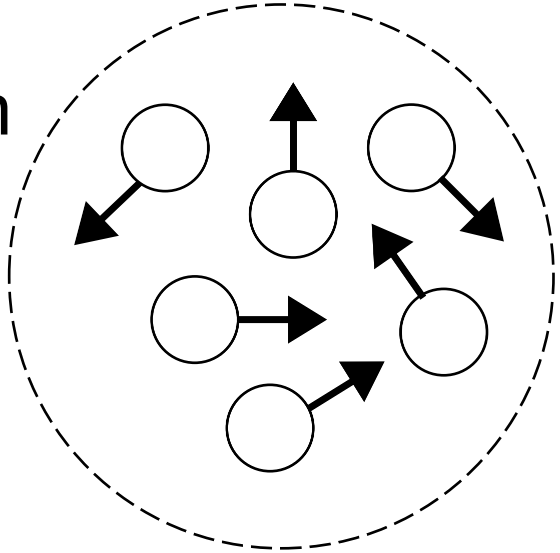
NUCLEAR SPIN - I

- I = j + s – sum of orbital angular momentum and spin angular momentum
- Multiplicity of states – 2I + 1
  - Nuclear spin quantum number *m* = -I, -I+1, … , I-1, I
- Energy of each state:

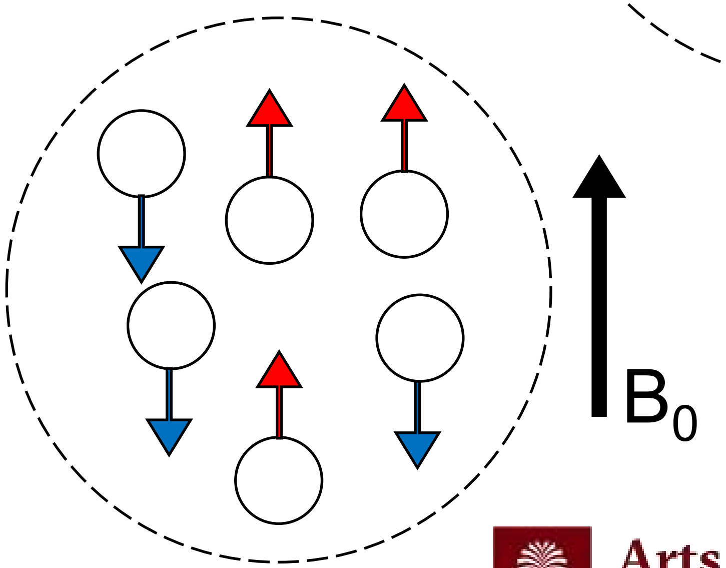
$$E_i = -m_i \frac{\gamma h B_0}{2\pi}$$

PARTICLES IN A MAGNETIC FIELD, B_0

- Start with population of nuclei in thermal equilibrium



- Degenerate nuclear spin states
- Random orientation
- Place in magnetic field – equal aligned and anti-aligned



BIG PROBLEM

- No net magnetization of population
- If $M = 0$, how can NMR be done?

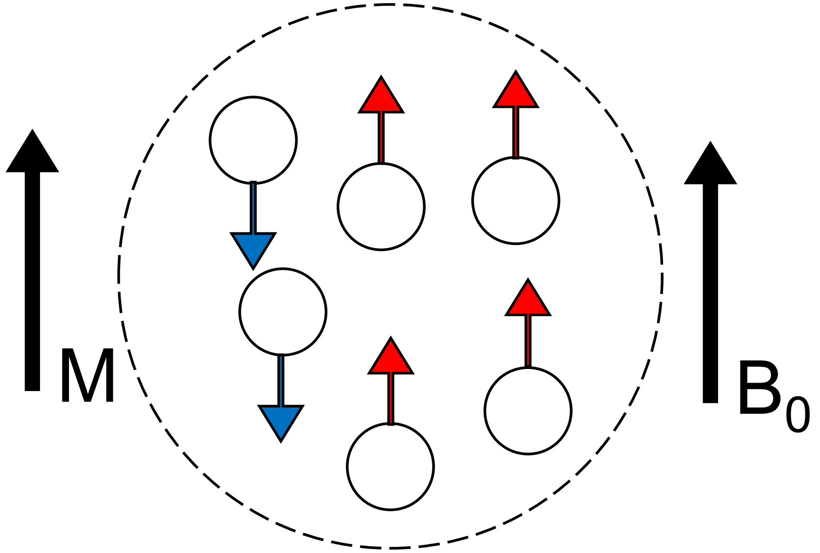
BOLTZMANN DISTRIBUTION

- Higher energy states less likely to be occupied

$$\frac{P_{m=-1/2}}{P_{m=1/2}} = e^{-\Delta E/kT}$$

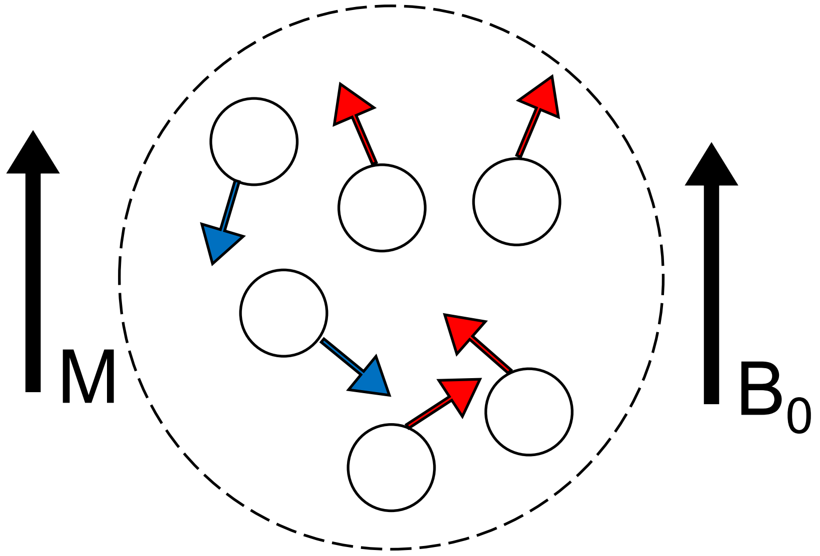
- More nuclei aligned with B_0 than anti-aligned

- Results in net magnetization



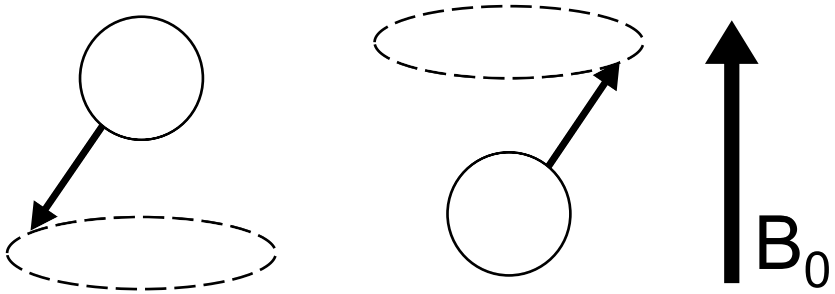
QUANTUM MECHANICS PROBLEM

- If each magnetic moment's direction is known, S_z is known
  - Knowing S_Z means S_x and S_y are also known
  - Violating uncertainty
- Each magnetic moment is off-axis
- Magnetization is unaffected



LARMOR PRECESSION

- Much like a spinning top, the nuclear spin will precess
  - Angular momentum
  - Torque due to B_0

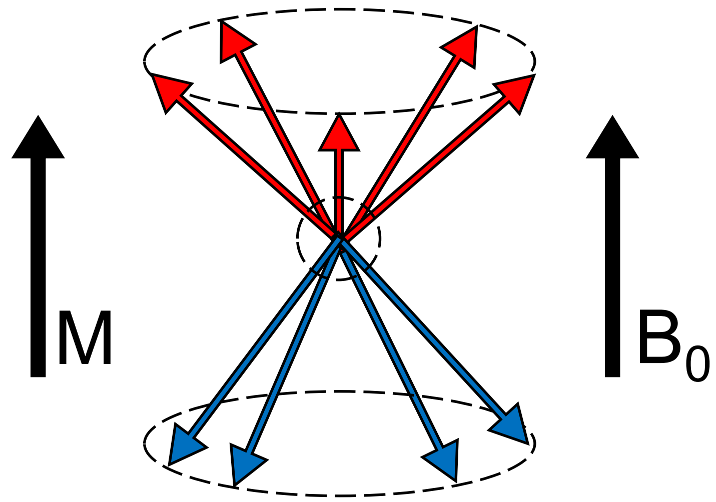


- Larmor frequency
  - Dependent only on *B* and the gyromagnetic ratio, gamma

$$\omega_0 = \gamma B$$

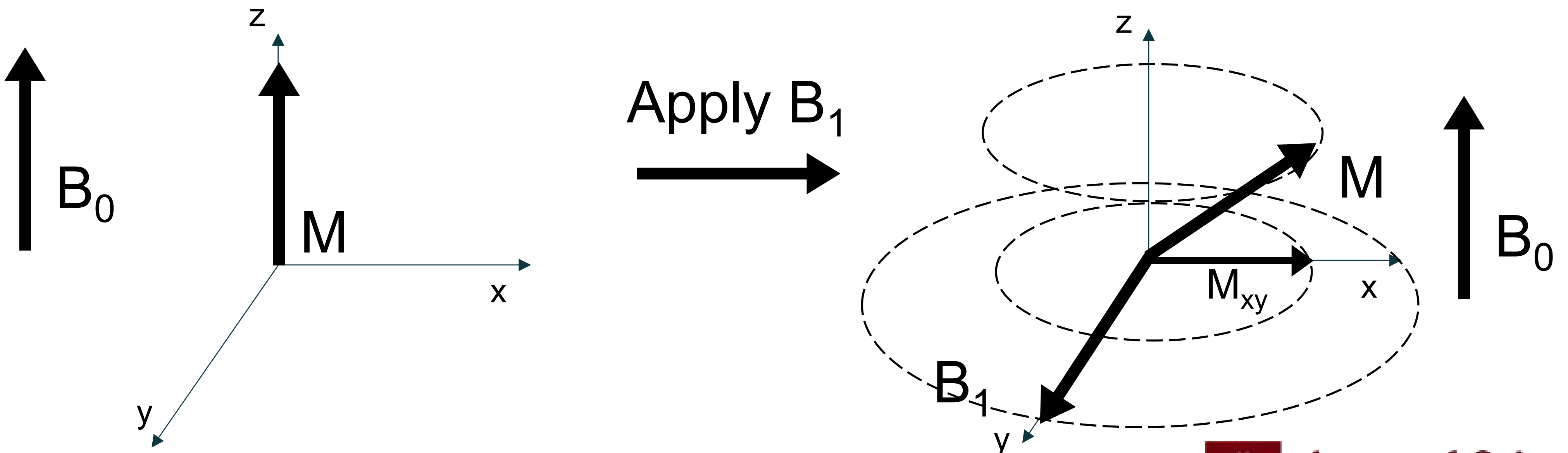
OVERVIEW

- Placing a population nuclei in a magnetic field results in a net magnetization aligned with the field
- Quantum mechanics causes each the magnetic moment of each nuclei to be off-axis and precess due to angular momentum and torque



SECONDARY OSCILLATING MAGNETIC FIELD

- Oscillates at the Larmor frequency
- Used to rotate magnetization to the x-y plane
- Resonant effect



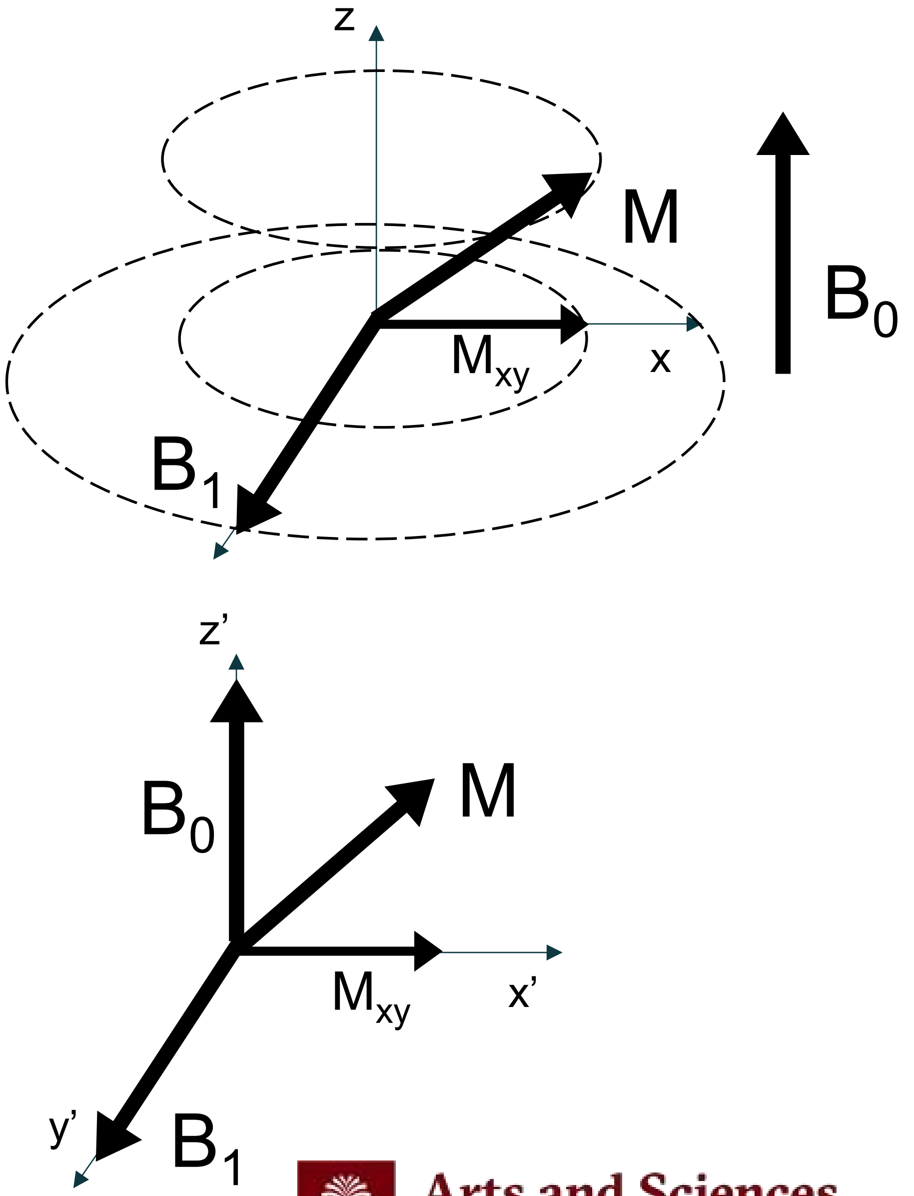
IMPORTANT CONSEQUENCE

- The Magnetization has a component now oscillating in the x-y plane

- This causes an induced current in nearby conductors via Faraday’s Law

ROTATING REFERENCE FRAME

- Reference frame denoted by x', y', z'
- Frame is rotating at the Larmor frequency
- Allows for more simple graphs and visualization



SPIN-SPIN (TRANSVERSE) RELAXATION

- Use resonant oscillating magnetic field to get magnetization perpendicular to applied field
- Describes time it takes for magnetization in x-y plane to decay back to 0
- Characterized by T_2 time

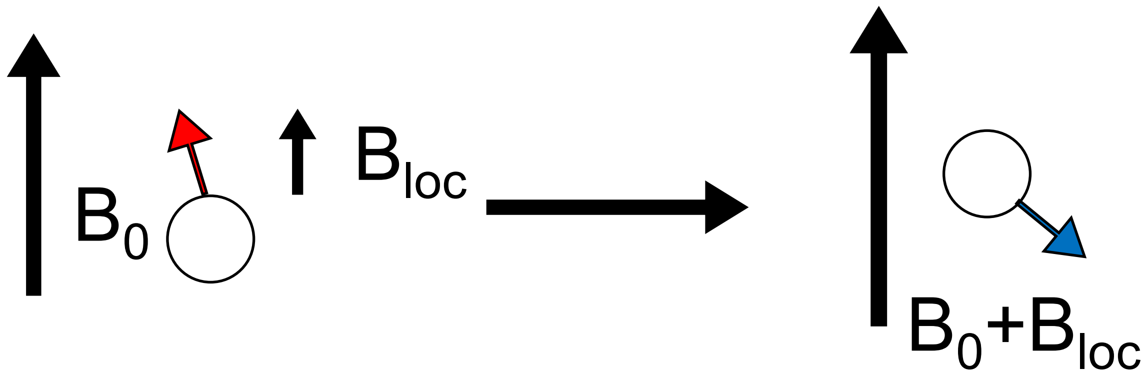
$$M_{xy}(t) = M_{xy}(0)e^{-t/T_2}$$

TRANSVERSE RELAXATION

- Processes that reduce the magnetization in the x-y plane contribute to transverse relaxation
- If fewer nuclei contribute towards the magnetization, then the magnetization decreases
- Processes that cause nuclei precessing with the magnetization to change their precession, contribute to transverse relaxation

TRANSVERSE RELAXATION PROCESS

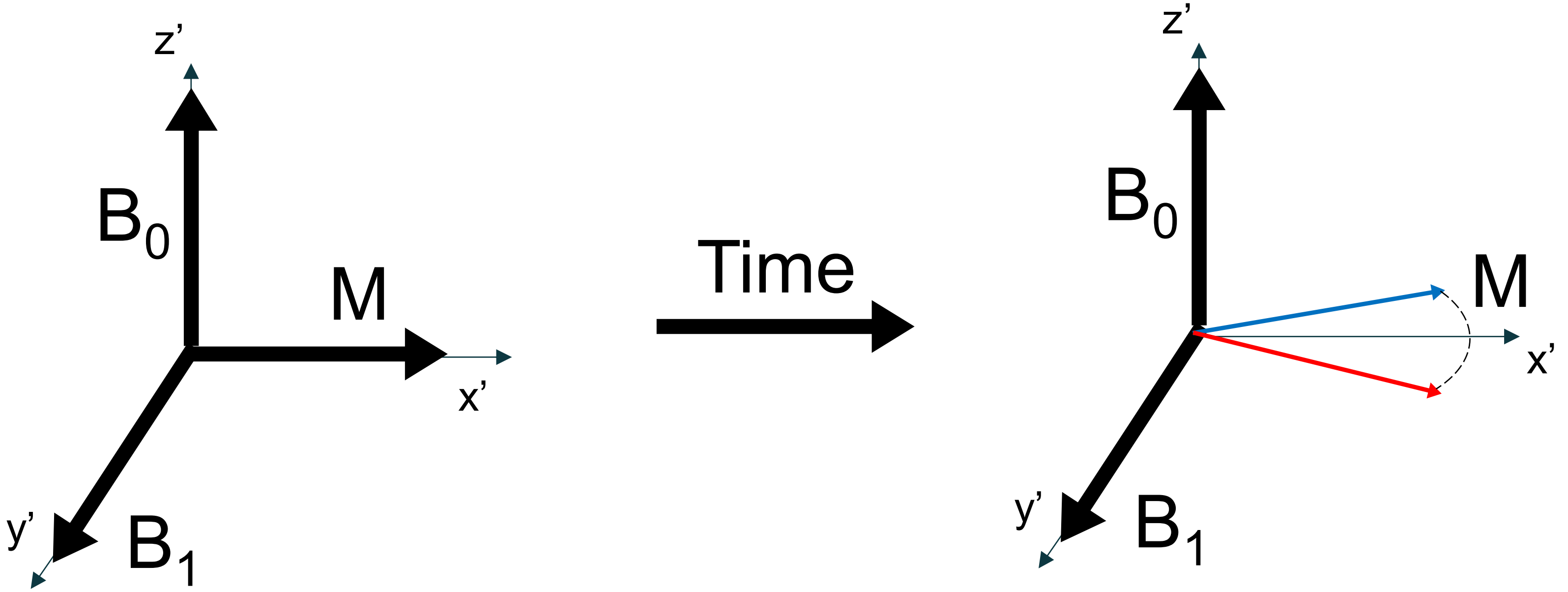
- Dipole-dipole interaction
  - Results in temporary increase/decrease in oscillation frequency
    - Loss of phase coherence
  - Strength dependent on gyromagnetic ratio
    - Electrons of paramagnetic material have much stronger interactions



$$\omega = \gamma(B_0 + B_{loc})$$

MEASURING TRANSVERSE RELAXATION

- Inhomogeneity in magnet causes differences in frequency for different nuclei
  - Causing a spread in rotating reference frame



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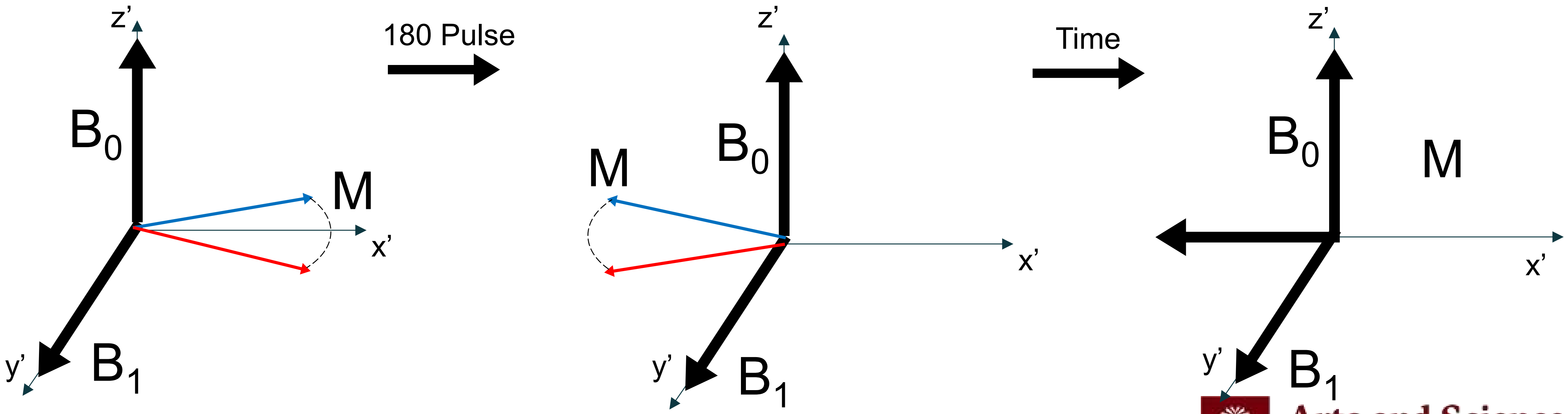
MEASURING TRANSVERSE RELAXATION

- Apply another oscillating magnetic field to rotate magnetization 180 degrees
  - Due to geometry the differences in frequencies will realign



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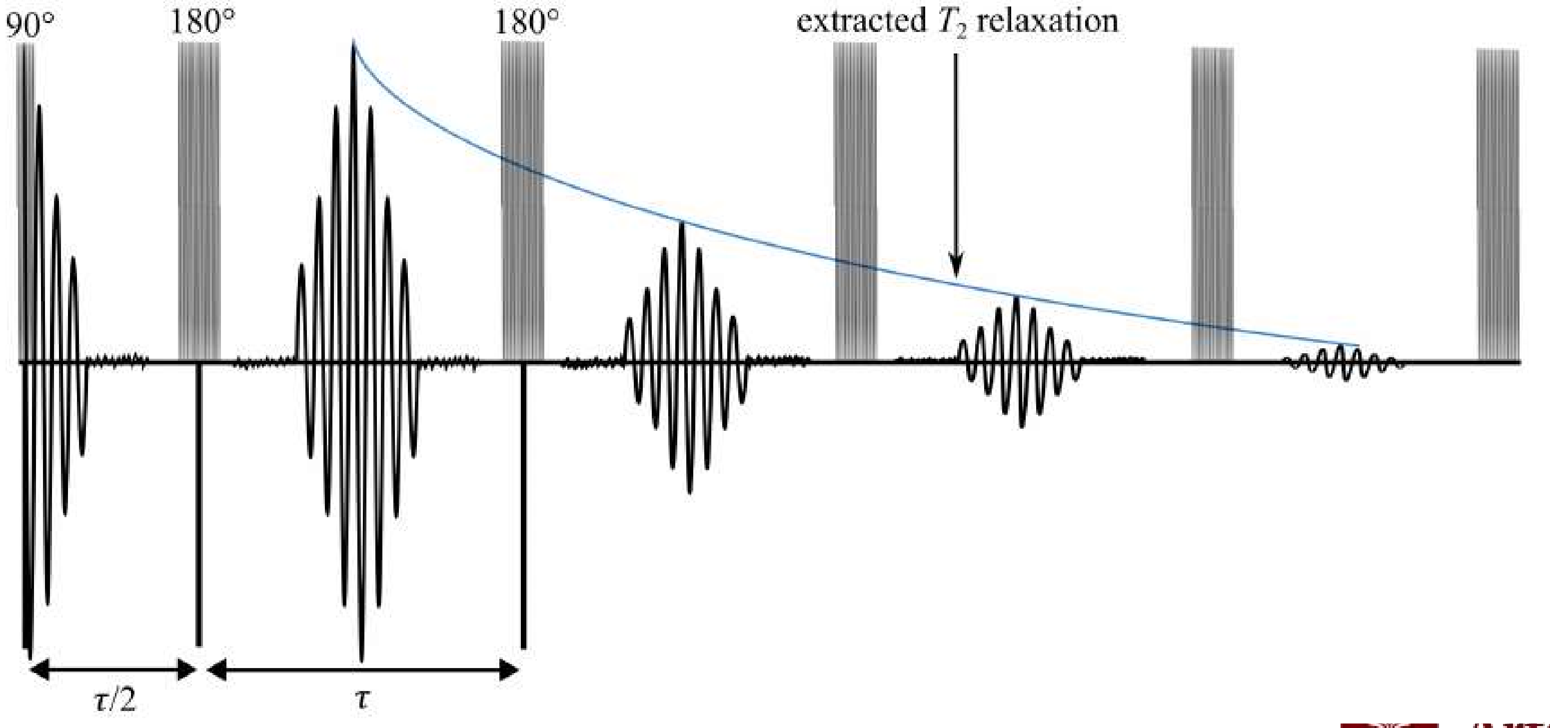
SPIN ECHOES

- Every time M_{xy} reaches its maximum



SIGNIFICANT RESULT

- **Transverse relaxation is unharmed by magnet inhomogeneities**

- This makes it perfect for small, portable magnets that are constrained by homogeneity

- NMR can be induced by an oscillating magnet field

- NMR signal can be observed via induced current

PAPER 1 GOAL: CREATE A CUSTOM COMPACT AND PORTABLE NMR SYSTEM

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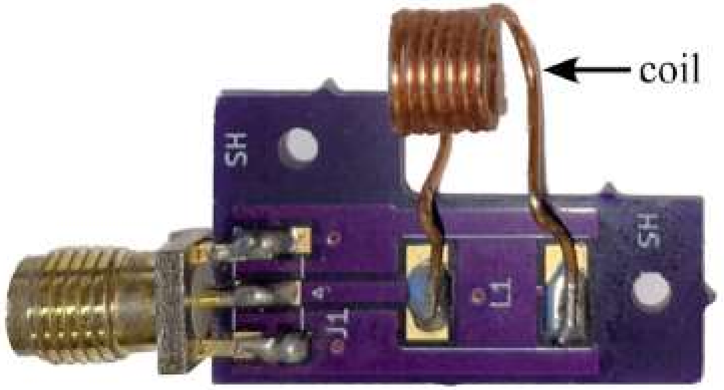
NMR COIL

- Produces oscillating magnetic field to generate NMR signal
- Receives NMR signal through induced current
- Most important piece of NMR system
- Allows measuring of T_2 time



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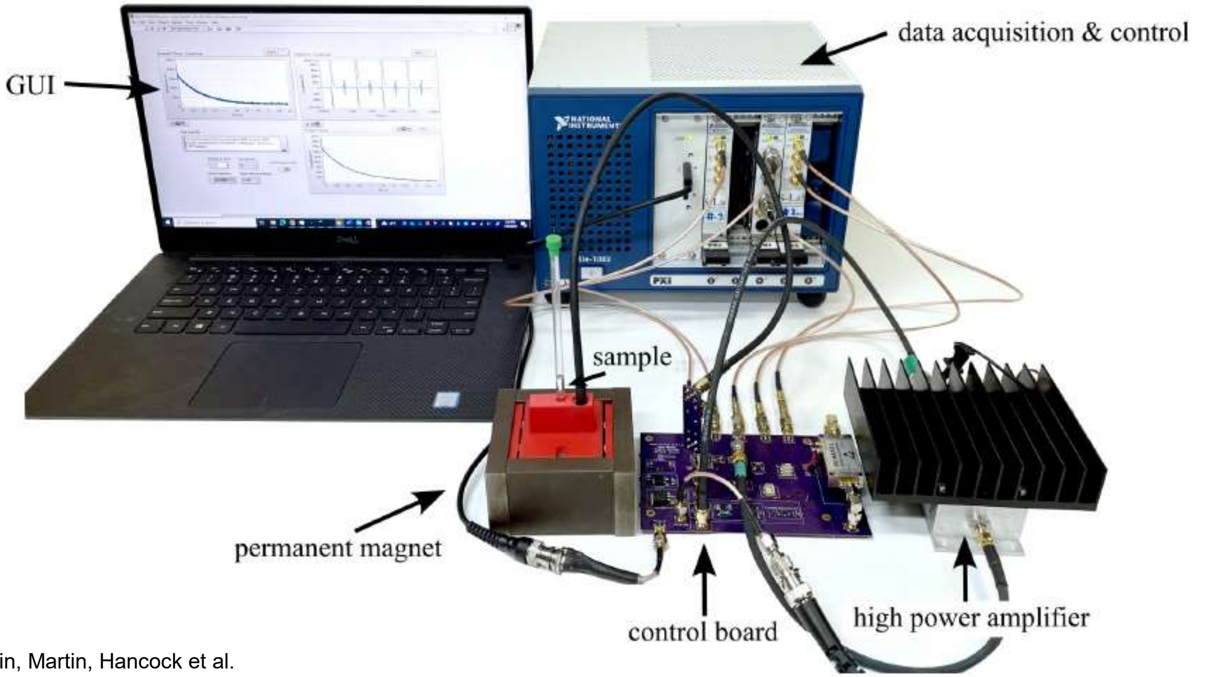
CUSTOM NMR SYSTEM

- Designed for radiofrequency (RF) applications
- Lots of filtering and amplification
- Utilizing National Instruments equipment to generate waveform required to generate NMR signal



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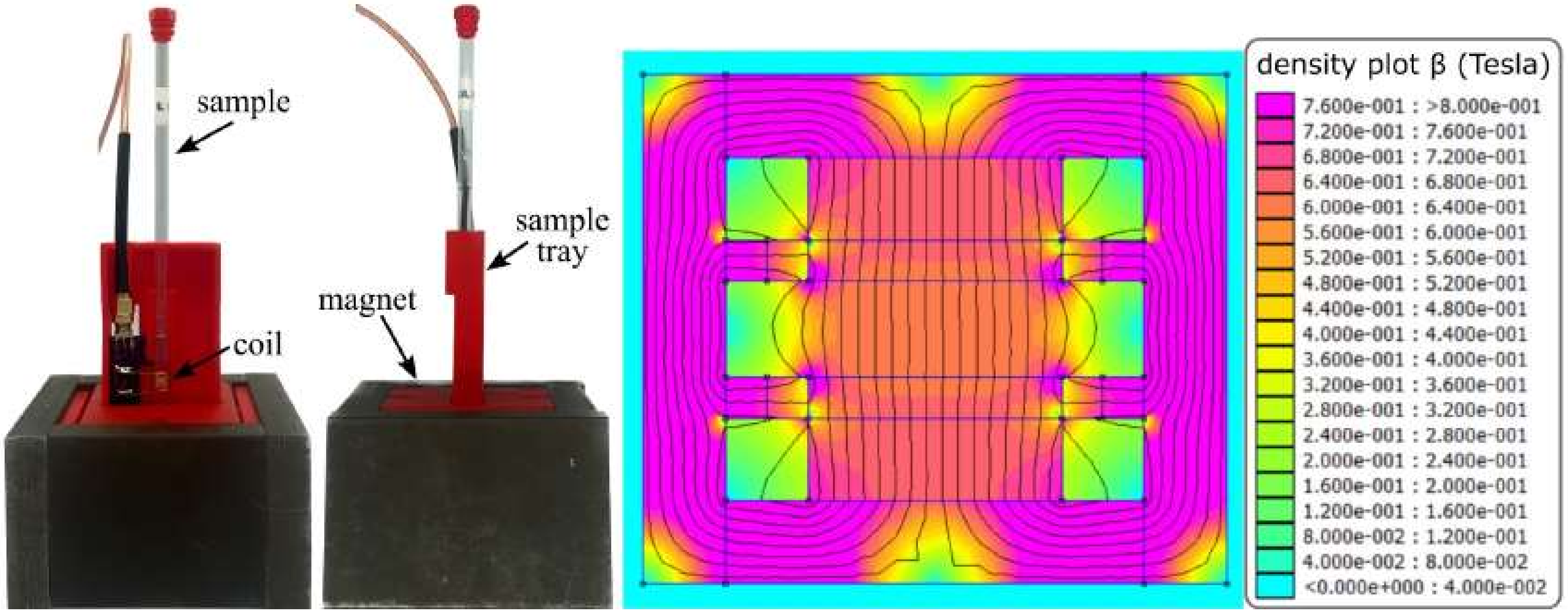
MAGNET DESIGN

- Designed to maximize simplicity, strength, and homogeneity



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THAT IS THE SYSTEM, WHAT CAN WE MEASURE WITH IT?

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MAGNETIC MATERIALS

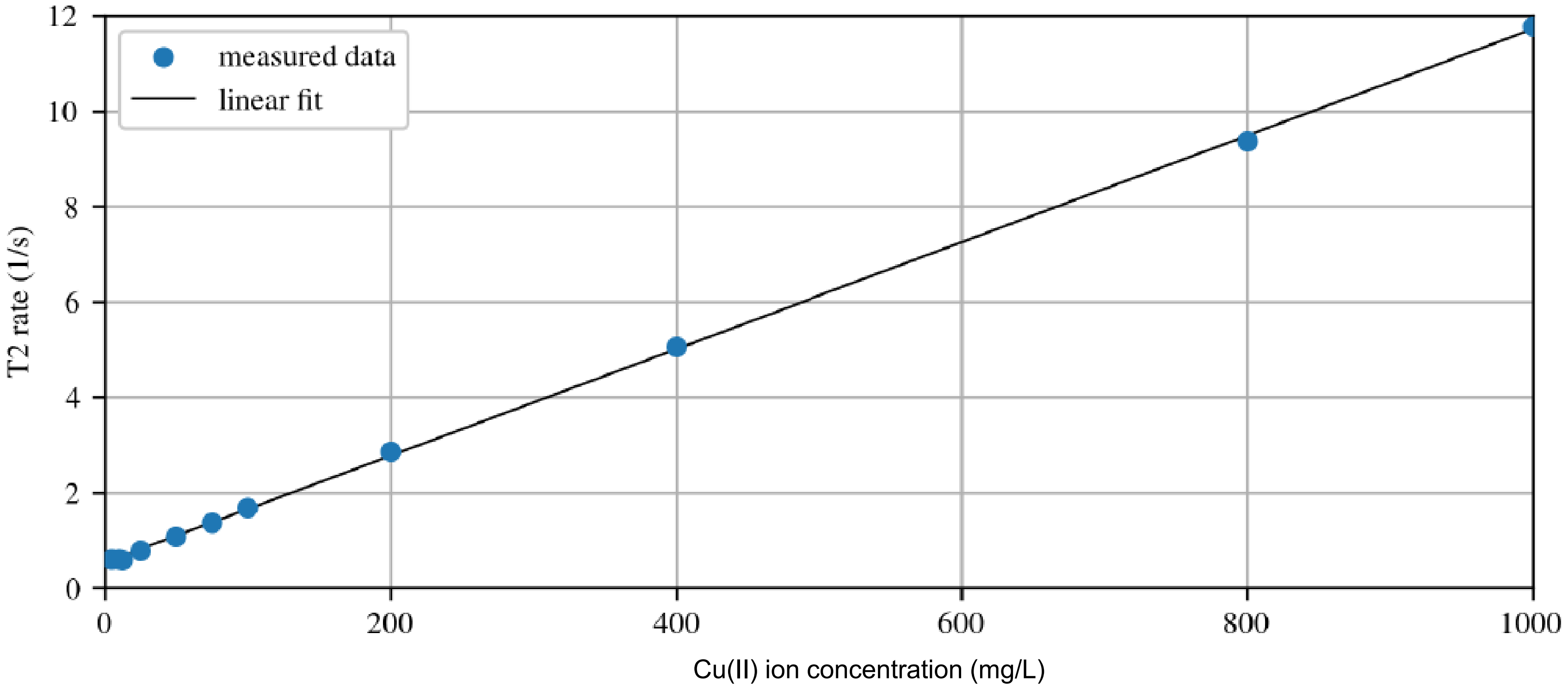
- Paramagnetic ions and solid particles
  - Cu(II), Ch(II), Mn(II), solid Al

- Environmental hazards, affecting wildlife and people

- Adding lots of small magnetic moments to the system
  - Affects the relaxation process
  - Linear relationship with T_2 rate

SYSTEM VALIDATION

- Test multiple concentrations of Cu(II) contaminated water



- R^2 of 0.998
- Less accurate data below 12 mg/L

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PAPER 2 GOAL: ADAPT SYSTEM FOR FIELD DEPLOYMENT AND ESTIMATE COPPER CONCENTRATION WITH DATA FROM FIELD DEPLOYMENT

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ADAPTATION FOR FIELD DEPLOYMENT

- Temperature Control
  - Magnet strength changes
  - RF electronic behavior changes
- Add pumps and tubing to transport new water
- Add an embedded controller
- Measure water quality data as well
  - Conductivity, pH, temperature

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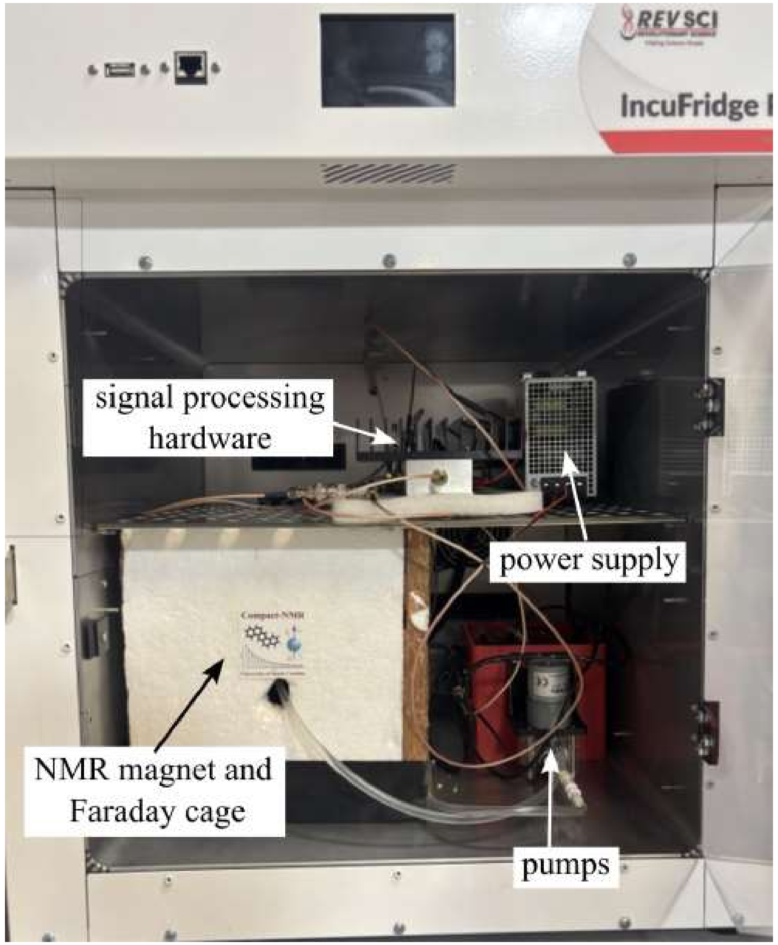
ADAPTATION FOR FIELD DEPLOYMENT

(a) (b)



GOAL

- Measure T_2 and water quality on different contamination concentrations of Cu(II)
- Train a ML model on the Cu(II) data
- Measure remotely at Rocky Branch Creek
- Use that model to predict magnetic content in Rocky Branch Creek

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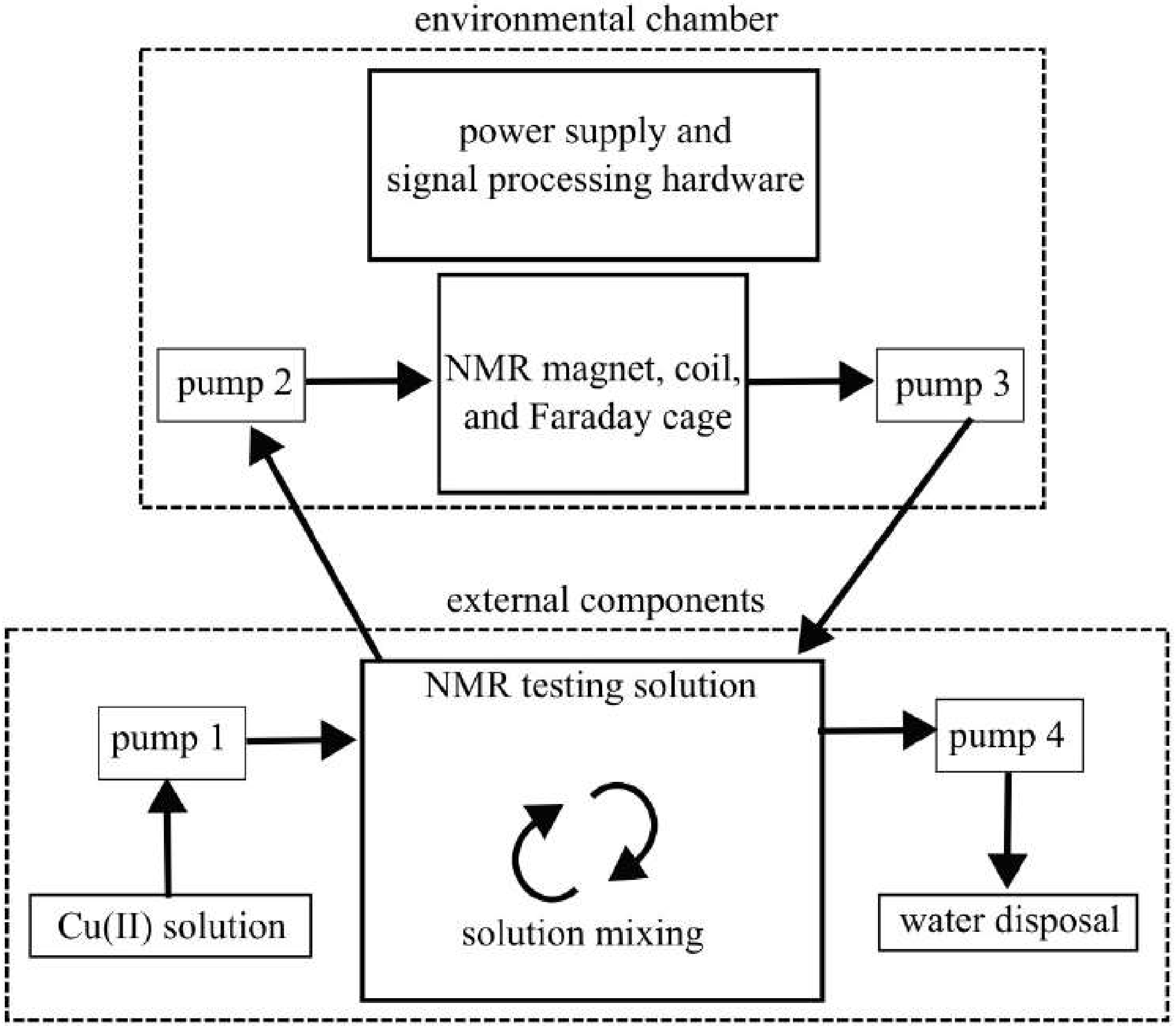
DATA COLLECTION

- Spread of copper contaminations from 0 mg/L to 1,000 mg/L
- Slow-drip providing near-continuous concentrations from 0 mg/L to 25 mg/L



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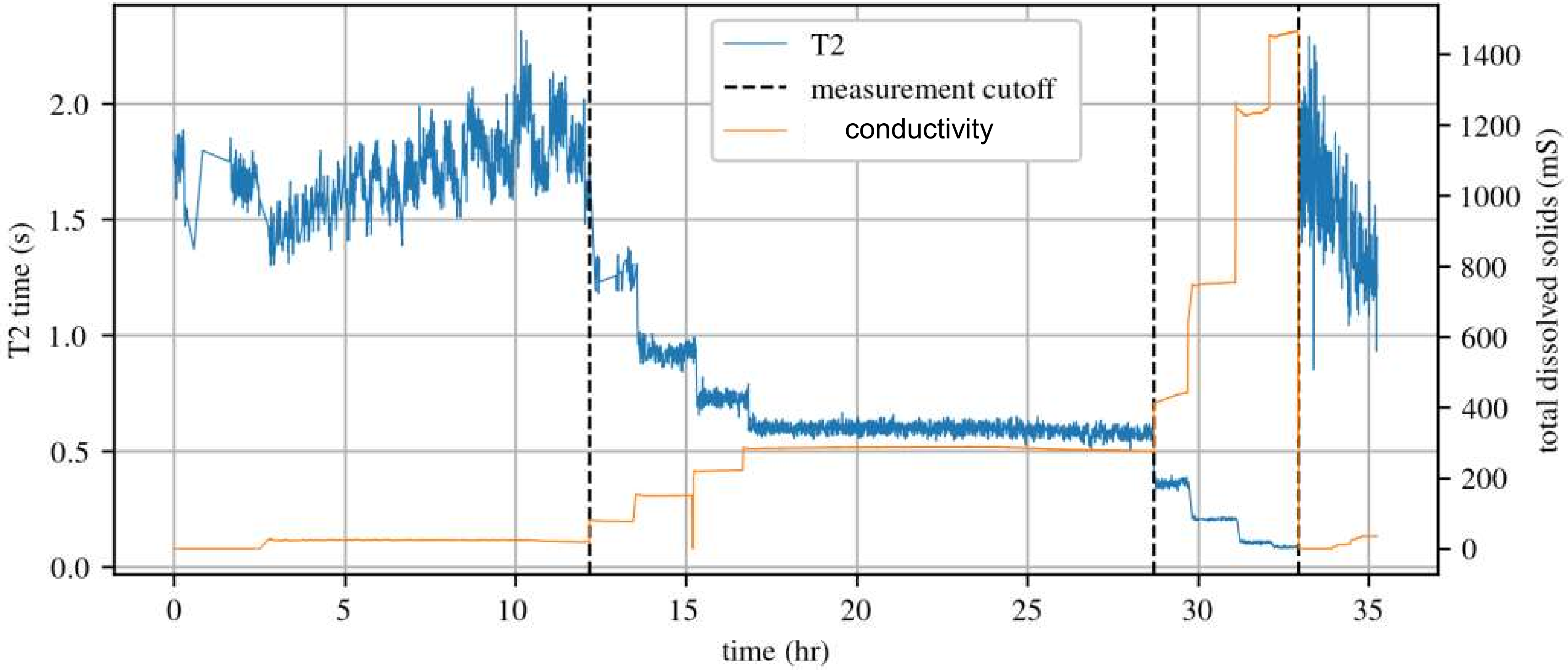
CU(II) DATA



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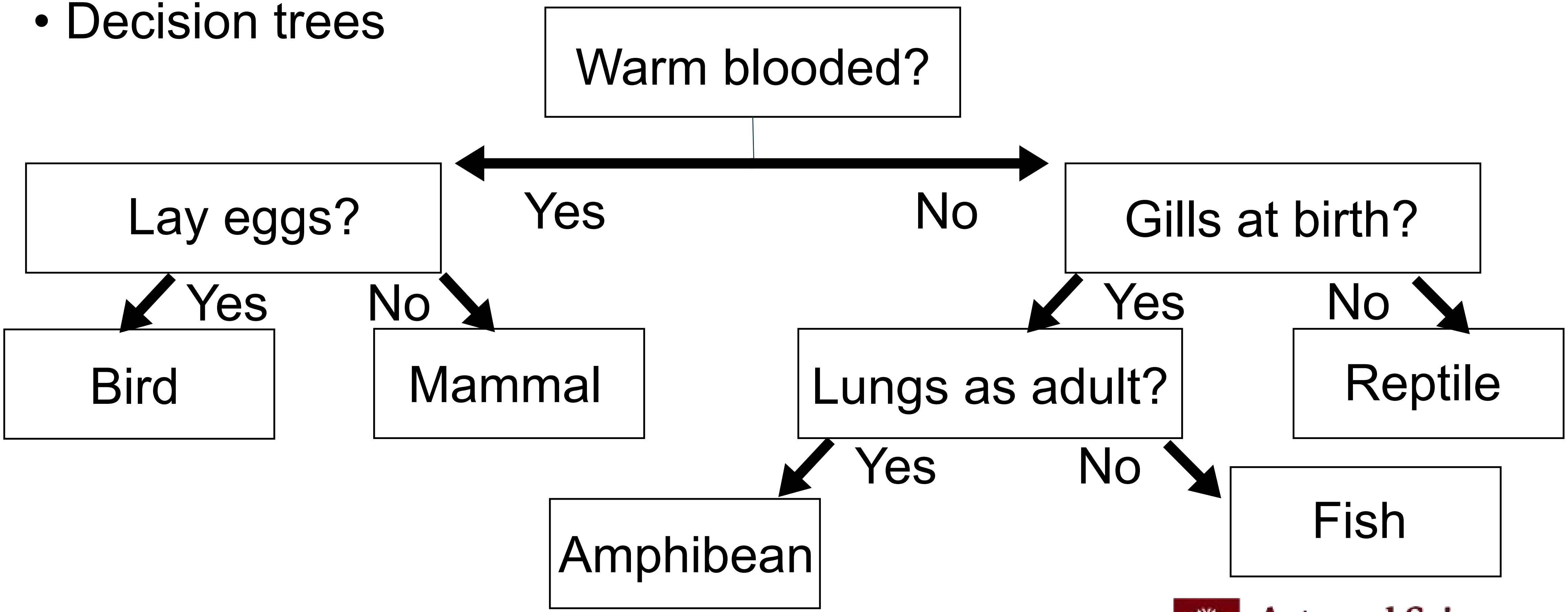
MACHINE LEARNING MODEL

- Decision trees



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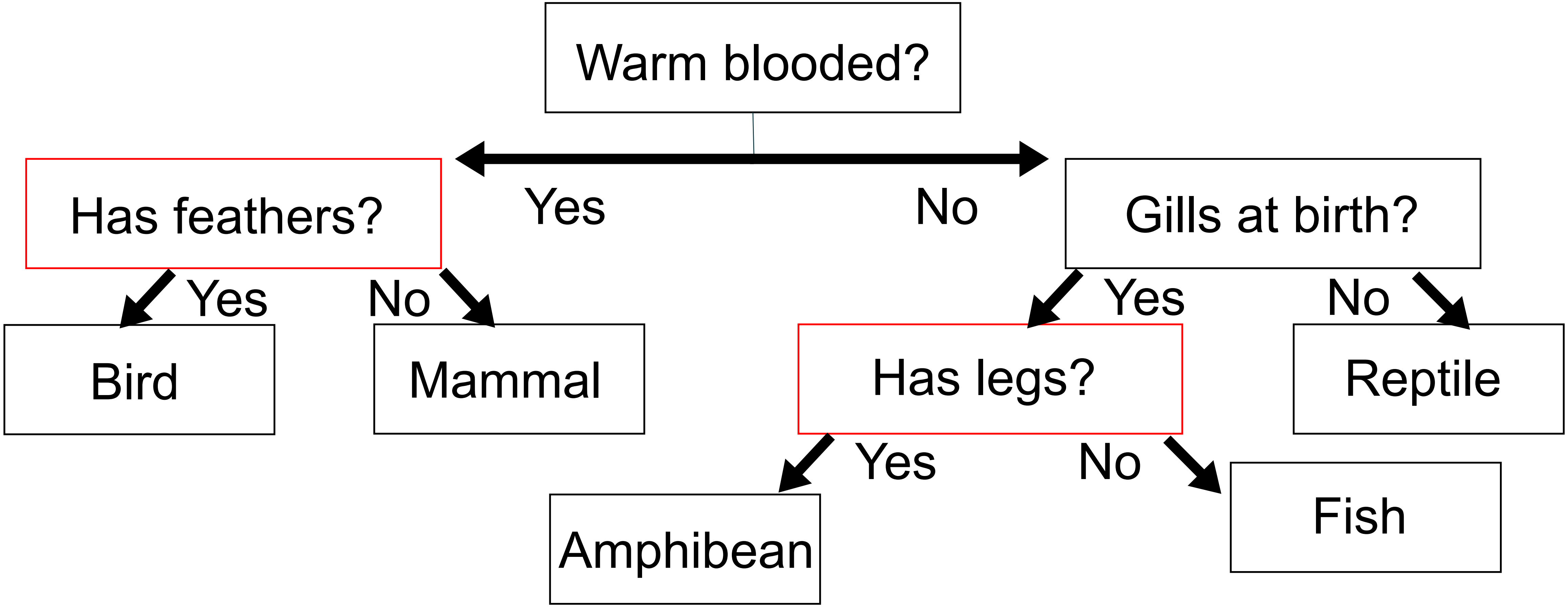

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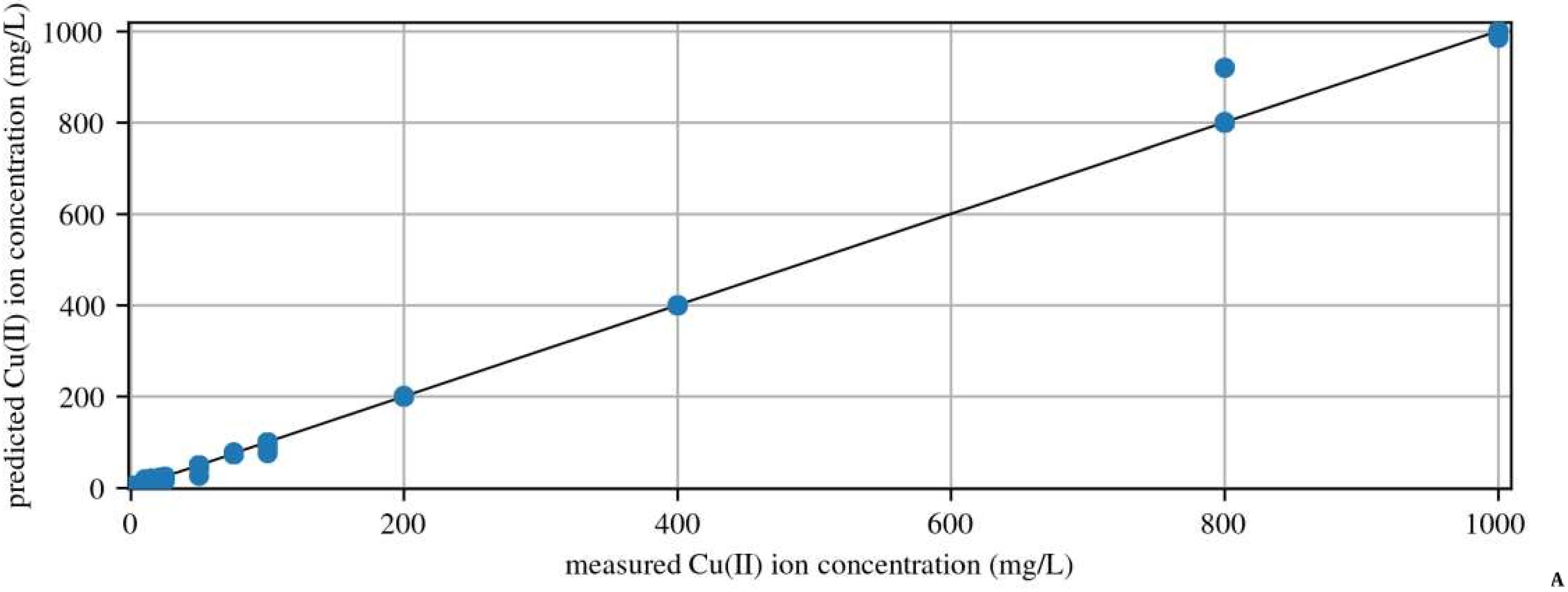
MACHINE LEARNING MODEL

- Random forest
  - Multiple decision trees, each with random sampling of training dataset

- Averages result from all trees

MODEL RESULTS

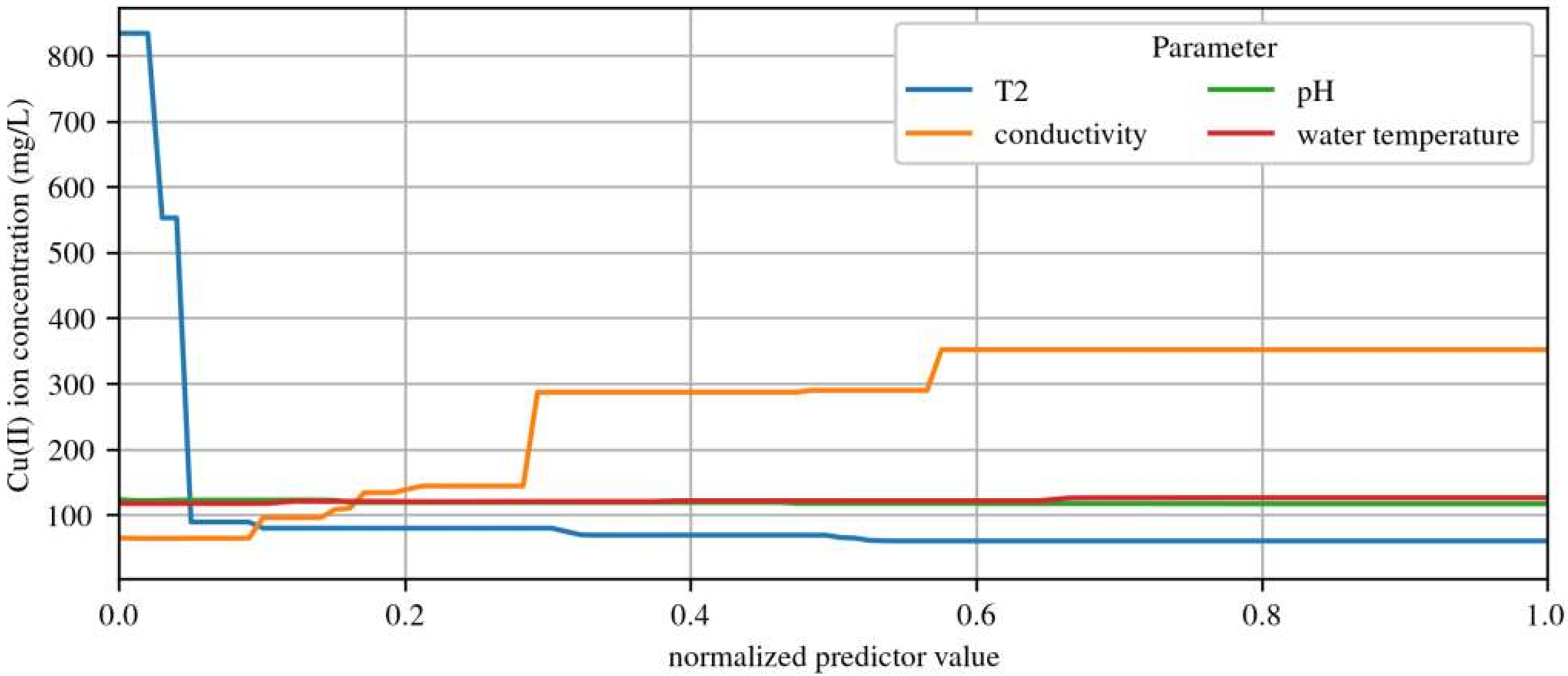
- Mean squared error of ~9 mg/L
- R^2 of 0.998



INTERPRETABILITY METHODS

- Partial dependence plot
  - Shows how each features affects the predicted value
- Feature importance
  - Shows how important each feature is to the model’s predictions

PARTIAL DEPENDENCE PLOT



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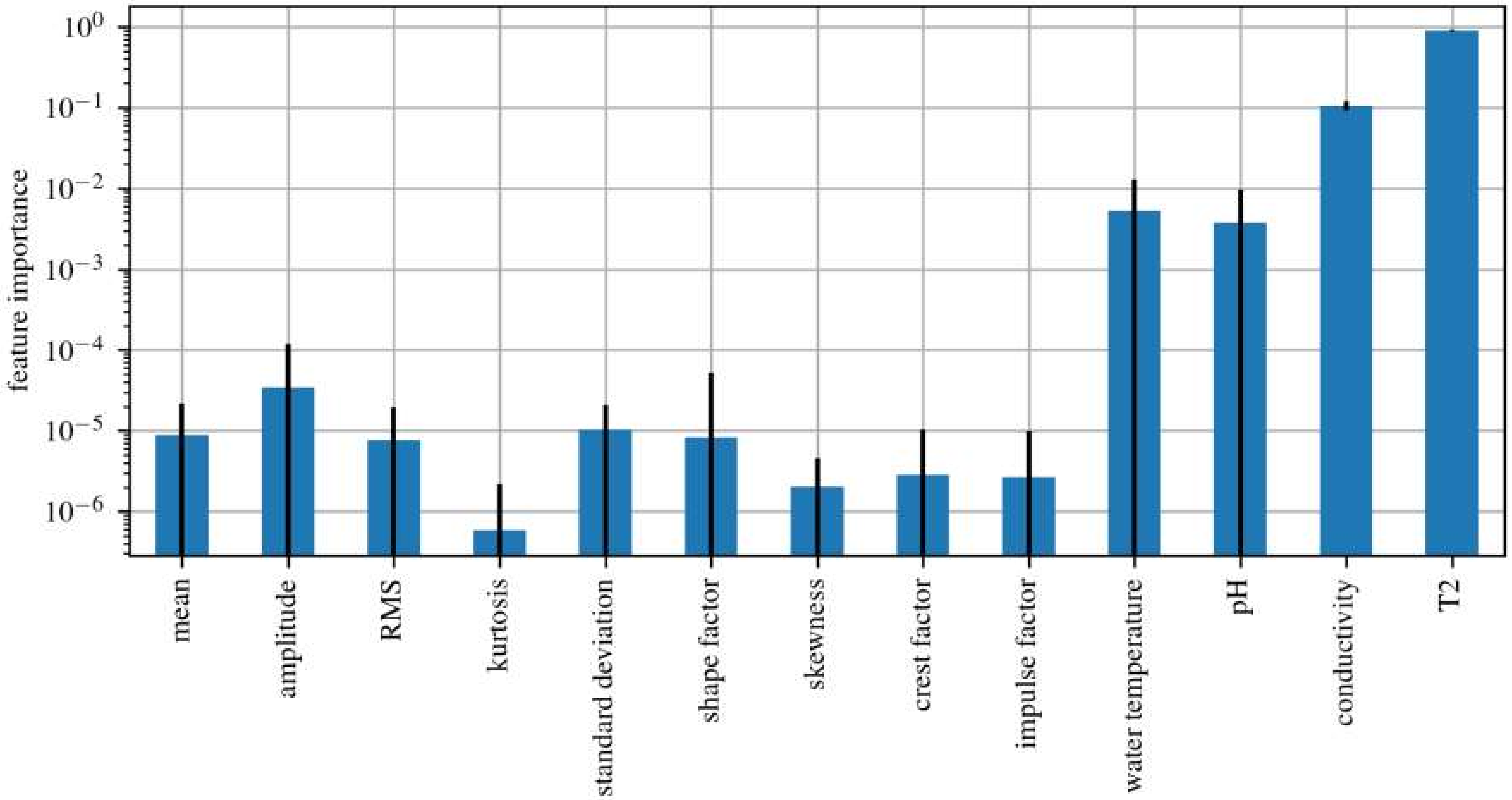
FEATURE IMPORTANCE PLOT



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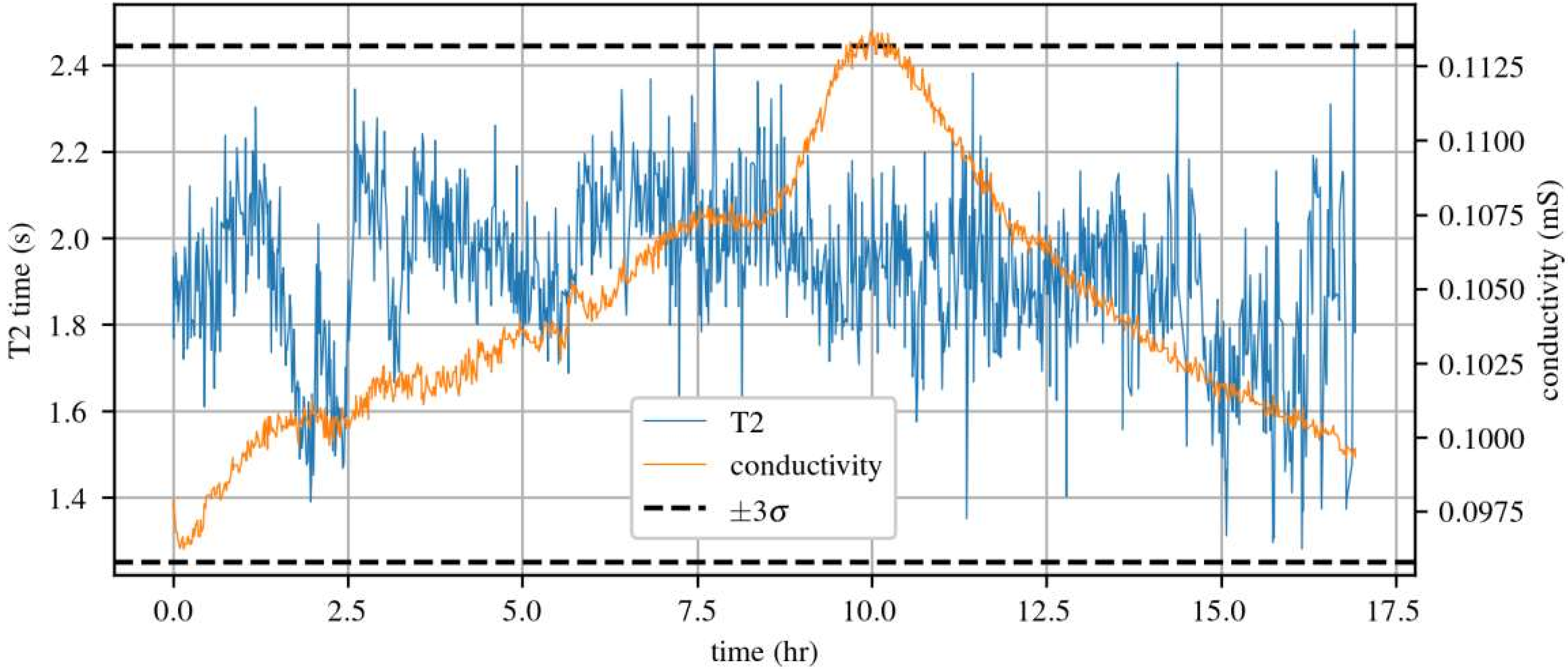
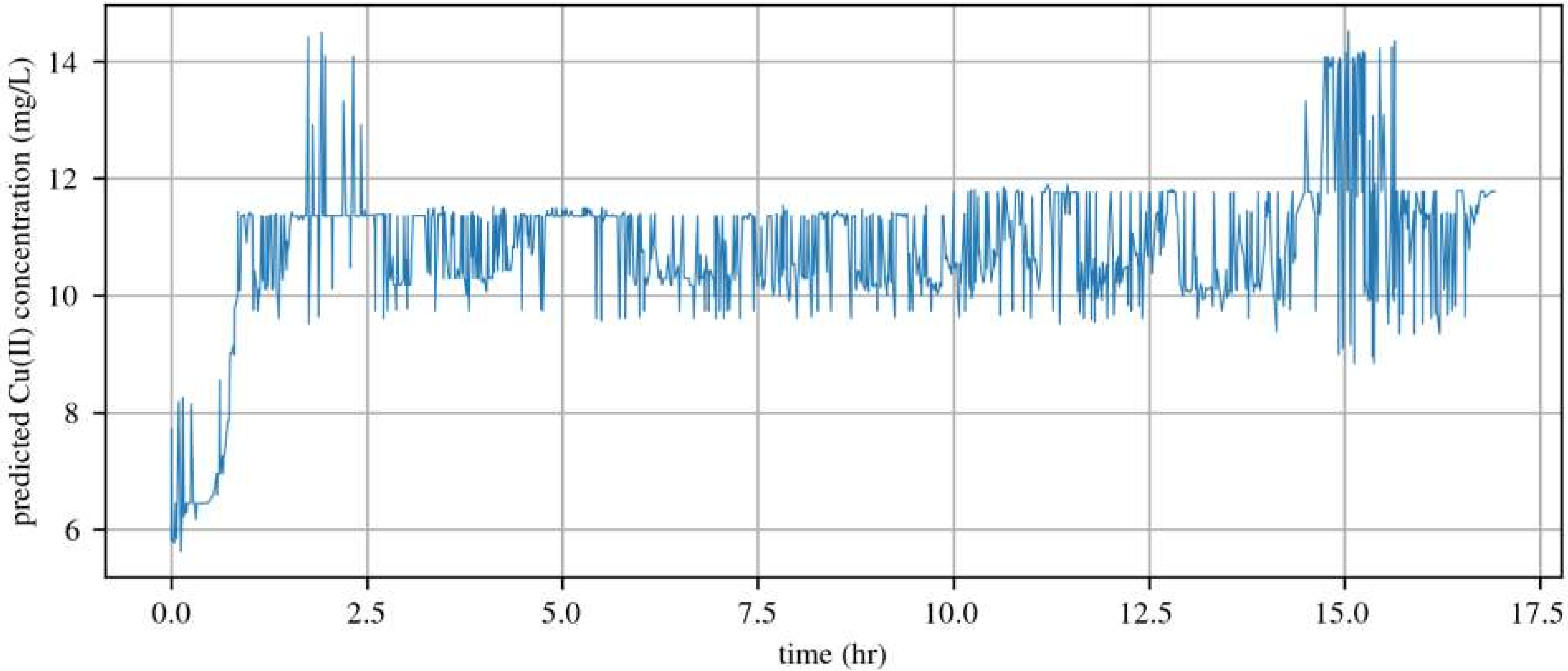
ROCKY BRANCH CREEK DATA



MODEL PREDICTIONS

- Model used to predict magnetic content from data from Rocky Branch Creek



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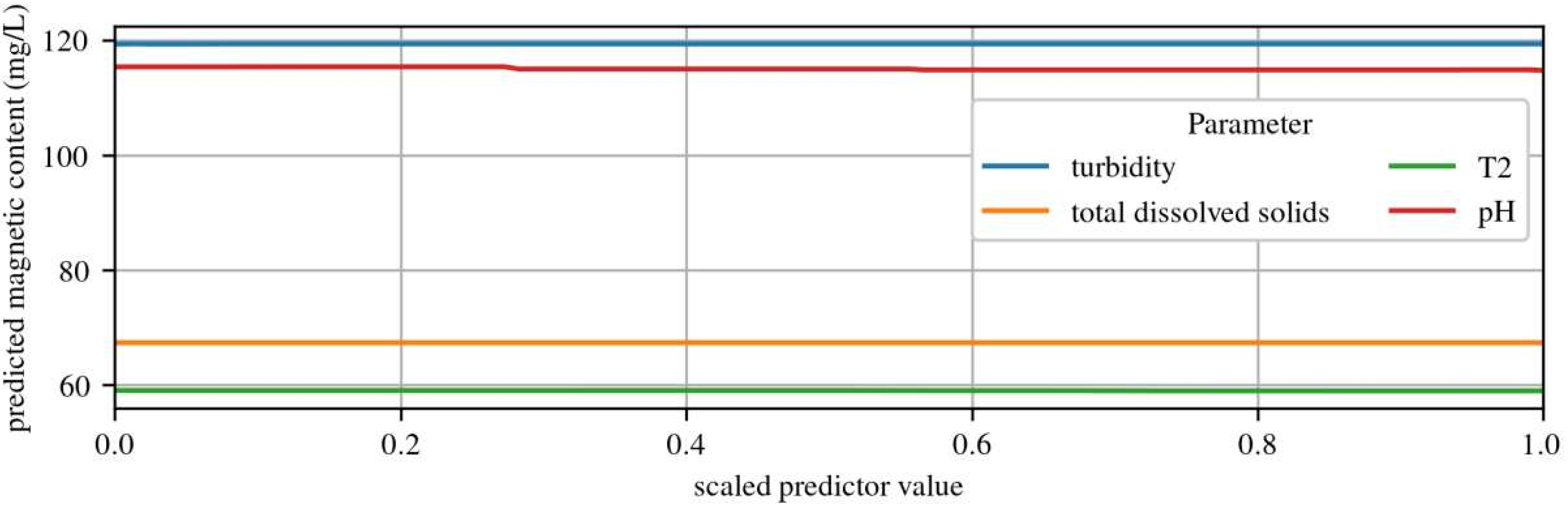
PREDICTION PDP



CONCLUSION

- Remote testing works great
- Fantastic results on training and test data
- Promising results on predictions
  - The predicted values are higher than expected
  - Other paramagnetic content?
  - Can we find a way to use Cu(II) training data to generalize paramagnetic content (magnetic moment per volume)

FUTURE WORK

- Look at using Cu(II) to generalize magnetic content
- Expand training and creek datasets
- Add ligands
  - Let us detect other materials

REFERENCES

Ismaila Abdullahi, *Magnetic resonance imaging of copper corrosion*, Ph.D. thesis, University of Birmingham, 2014.

Belal M.K. Alnajjar, André Buchau, Lars Baumgärtner, and Jens Anders, *Nmr magnets for portable applications using 3d printed materials*, **326**, 106934.

Yoshimi Anzai and Linda Moy, *Point-of-care low-field-strength mri is moving beyond the hype*, **305**, no. 3, 672–673.

ARTS-Lab, *Compact-NMR*, GitHub.

Santosh Kumar Bharti and Raja Roy, *Quantitative 1H NMR spectroscopy*, **35**, 5–26.

Bernhard Blümich, *Introduction to compact NMR: A review of methods*, **83**, 2–11.

Bernhard Blümich and Kawarpal Singh, *Desktop NMR and its applications from materials science to organic chemistry*, **57**, no. 24, 6996–7010.

Bernhard Blümich, Christian Rehorn, and Wasif Zia, *Magnets for small-scale and portable NMR*, pp. 1–20.

Peter Blümler and Helmut Soltner, *Practical concepts for design, construction and application of halbach magnets in magnetic resonance*, **54**, no. 11–12, 1701–1739.

Nicholas Bryden, Michael Antonacci, Michele Kelley, and Rosa T. Branca, *An open-source, low-cost NMR spectrometer operating in the mT field regime*, **332**, 107076.

H. Y. Carr and E. M. Purcell, *Effects of diffusion on free precession in nuclear magnetic resonance experiments*, Phys. Rev. **94** (1954), 630–638.

Janvrin, Winford and Martin, Jacob and Hancock, Daniel and Downey, Austin and Pellechia, Perry and Satme, Joud and Won, Sang Hee, *Open-Source Compact Time-Domain Hydrogen (1h) Nmr System for Field Deployment, 2025*

Melvina C. Ezeanaka, John Nsor-Atindana, and Min Zhang, *Online low-field nuclear magnetic resonance (lf-nmr) and magnetic resonance imaging (mri) for food quality optimization in food processing*, **12**, no. 9, 1435–1451.

Parker Huggins, Win Janvrin, Jake Martin, Ashley Womer, Austin R. J. Downey, John Ferry, Mohammed Baalousha, and Jin Yan, *Assessing magnetic particle content in algae using compact time domain nuclear magnetic resonance*, Ocean Sensing and Monitoring XVI (Weilin Hou and Linda J. Mullen, eds.), vol. 6, SPIE, p. 1.

Parker Huggins, Jacob S. Martin, Austin R.J. Downey, and Sang Hee Won, *Interpretable machine learning for predicting the derived cetane number of jet fuels using compact TD-NMR*, 137018.

S Iguchi, R Piao, M Hamada, S Matsumoto, H Suematsu, T Takao, A T Saito, J Li, H Nakagome, X Jin, M Takahashi, H Maeda, and Y Yanagisawa, *Advanced field shimming technology to reduce the influence of a screening current in a rebco coil for a high-resolution NMR magnet*, Superconductor Science and Technology **29** (2016), no. 4, 045013.

National Instruments, *Pxi-5124 specifications*, February 2023.

Simon Kern, Klas Meyer, Svetlana Guhl, Patrick Graber, Andrea Paul, Rudibert King, and Michael Maiwald, *Online low-field NMR spectroscopy for process control of an industrial lithiation reaction-automated data analysis*, **410**, no. 14, 3349–3360.

Alain Louis-Joseph and Philippe Lesot, *Designing and building a low-cost portable FT-NMR spectrometer in 2019: A modern challenge*, **22**, no. 9-10, 695–711.

Jacob Martin, Austin R.J. Downey, and Sang Hee Won, *Compact time domain NMR design for the determination of hydrogen content in gas turbine fuels*, Volume 1: 24th International Conference on Advanced Vehicle Technologies (AVT), American Society of Mechanical Engineers, aug 2022.

Jacob S. Martin, Austin R. J. Downey, Mohammed Baalousha, and Sang Hee Won, *Rapid measurement of magnetic particle concentrations in wildland-urban interface fire ashes and runoff using compact NMR*, **24**, no. 6, 7355–7363.

David C. Meeker and M Priboianu, *Finite element method magnetics*, 2002.

Giorgio Moresi and Richard Magin, *Miniature permanent magnet for table-top NMR*, Concepts in Magnetic Resonance Part B: Magnetic Resonance Engineering **19B** (2003), no. 1, 35–43.

Sarah Mandy Nagel, Christoph Strangfeld, and Sabine Kruschwitz, *Application of 1h proton NMR relaxometry to building materials - a review*, **6-7**, 100012.

The Electronic Code of Federal Regulations, *Part 18—industrial, scientific, and medical equipment*, February 2025.

Dmytro Polishchuk and Han Gardeniers, *A compact permanent magnet for microflow NMR relaxometry*, **347**, 107364.

H. Raich and P. Blümler, *Design and construction of a dipolar halbach array with a homogeneous field from identical bar magnets: NMR mandhalas*, **23B**, no. 1, 16–25.

Veer Singh, Nidhi Singh, Sachchida Nand Rai, Ashish Kumar, Anurag Kumar Singh, Mohan P. Singh, Ansuman Sahoo, Shashank Shekhar, Emanuel Vamanu, and Vishal Mishra, *Heavy metal contamination in the aquatic ecosystem: Toxicity and its remediation using eco-friendly approaches*, Toxics **11** (2023), no. 2, 147.

Sudarningsih Sudarningsih, Aditya Pratama, Satria Bijaksana, Fahruddin Fahruddin, Andi Zanuddin, Abdus Salim, Habib Abdillah, Muhammad Rusnadi, and Mariyanto Mariyanto, *Magnetic susceptibility and heavy metal contents in sediments of riam kiwa, riam kanan and martapura rivers, kalimantan selatan province, indonesia*, Heliyon **9** (2023), no. 6, e16425.

Michael C.D. Tayler and Sven Bodenstedt, *Nmrduino: A modular, open-source, low-field magnetic resonance platform*, **362**, 107665.

David Wamai, *signal-processing-instrument-for-nmr*, February 2025.

Lizhi Xiao, Guangzhi Liao, Feng Deng, Huabing Liu, Gongpu Song, and Mengchun Li, *Development of an NMR system for down-hole porous rocks*, **205**, 16–20.

THANKS!

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